

Waterborne Silicates in Coatings and Construction Chemicals

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AUTHOR PROFILE

Adrian Thomas was born in England and graduated with B.Sc (Hons) from the University of Southampton in 1969 prior to transferring to Australia. In Australia he has had extensive experience with a number of multinational companies (including Unilever, Shell and Wacker Chemicals) in a range of manufacturing, sales and marketing positions at management levels.

His professional memberships include: American Chemical Society, Royal Australian Chemical Institute; Royal Society of Chemistry, United Kingdom; Australian Marketing Institute; Australasian Corrosion Association; Australian Society of Cosmetic Chemists and Surface Coatings Association Australia (SCAA).

His commercial activities include consulting in areas including technical consulting and regulatory affairs consulting as well as trading in a range of raw material chemicals for industries including the surface coatings industry. Chemicalia is the distributor in Australia and New Zealand of waterborne silicates from Woellner GmbH & Co. KG in Germany.

Overview:

Waterborne alkali silicates have a long history in coatings applications, but particularly in overseas markets such as Europe have gained greater prominence since the 1970s in the form of silicate emulsion coatings (also known as organo-silicate coatings).

In this paper the history, production, formulation and applications of waterborne alkali silicates are discussed in areas such as:

- Silicate coatings
- Silicate impregnations
- Silicate emulsion coatings
- Silicate emulsion plasters

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End markets for these products include:

- Architectural coatings
- Architectural renders
- Waterborne zinc rich protective coatings
- Masonry impregnation
- Waterborne consolidating primer
- Chemical damp-proofing

Silicate coatings are typically 2-component coatings (sometimes referred to as 2-K coatings) which have been used in Europe for architectural coatings since the late 1870's. Although still being used now, they suffer from the disadvantages of requiring mixing and permitting to mature before application

Victor Nightingall essentially started the industry of 2-K inorganic zinc coatings in Melbourne during the 1940s. These were initially based on waterborne alkali silicate resins mixed with high proportions of zinc dust (essentially an analogue of the earlier 2-component coatings, although based on different pigments and designed for anticorrosive applications rather than architectural applications). Subsequently these coatings were replaced by solventborne ethyl silicates and were adopted in other parts of the World, particularly throughout USA and Europe. During recent times, with the reduction in VOC content of coatings, developments have returned to zinc rich silicate coatings based on waterborne silicates, essentially a case of the wheel of progress turning full circle!

Silicate impregnations may be and are being used in a number of areas including:

- The impregnation of concrete to achieve surface hardening
- The consolidation of weathered natural stone
- The incorporation of a chemical damp-proof course to act as a barrier against damp, particularly rising damp

Silicate emulsion coatings were first introduced into the market in Europe in the 1960s, coming to prominence in the 1970s. With the experience of long-term stability of exterior coatings based on 2-K silicate paints as well as the benefits of organic emulsion paints with their attractiveness, ease of production and good storage stability, there was a desire for a single pack (1-K) coating system to exhibit the properties of mineral paints together with ease of production, ease of application and good storage stability. Requirements of such a 1-K coating system were to include the following:

- Ready-to-use products
- Easy and fairly quick production
- Proper rheological behaviour
- Stabilization of binder - filler/pigment system against reagglomeration
- Good storage stability (shelf life at least one year)
- Small degree of syneresis and sedimentation
- Good redispersibility on stirring
- Good application properties
- Sufficient diffusion into substrate for strong adhesion and surface hardening
- Good and equal colour retention on the substrate
- Perfect curing without chalking
- Good weathering stability
- Maintenance of easy water vapour permeation

The above properties were achieved using appropriately formulated systems based on stabilised potassium silicate binders, blended with small proportions of alkali stable organic emulsion resins, with appropriately selected pigments and additives.

About 10-15% of the waterbased architectural paint market in Europe is based on silicate emulsion paints. Introduction into other markets including United States of America, Asia and Australasia is occurring at the present.

In a similar fashion, silicate emulsion renders based on similarly selected binders and resins may be formulated using appropriately selected fillers such as those based on calcium carbonate or silica.

Waterborne alkali silicates in coatings are believed to be harmless to the environment on the basis that:

- The cured systems are silicate based, which are effectively very close to what already exists in Nature
- According to the criteria of the Australian NOHSC (National Occupational Health and Safety Commission) are not hazardous substances
- According to the criteria of the ADG-7 (Australian Dangerous Goods Code, 7th edition) waterborne alkali silicates are not Dangerous Goods

Also waterborne alkali silicates:

- Exhibit no significant health risk during application
- Have no allergenic potential from silicate binders
- Are zero VOC products
- Can provide a good economic lifetime of the coating (leading to less requirement to reapply the coating) due to long term stability

1. Silicates occurring in Nature.

In Nature, it is understood that more than 95 vol% of the earth's crust is composed of quartz and a few rock-forming silicates. These include:

- Plagioclase, $\text{Na}(\text{AlSi}_3\text{O}_8)$ - $\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$ 42% by volume
- Potassium Feldspars KAlSi_3O_8 - 22% by volume
- Quartz (or Silica) SiO_2 – 18% by volume

Other more complex silicates include Amphibole at 5% by volume and other silicates at 12% by volume. Silicon compounds are also present in the hydrosphere, mainly as dissolved silica. Also, a large number of silicates have been identified in extraterrestrial material.

It is understood that Man as far back as 600,000 years ago has been using silica in the form of flint (which is a cryptocrystalline silica called chert). In this form the crystals are so fine as to be indistinguishable except under powerful magnification.

So it is probably appropriate to suggest that as materials "Silicates are very close to Nature".

However for our particular discussion we are focused on soluble silicates (in particular on waterborne alkali silicates) which may be used in applications such as coatings and construction chemicals.

2. History of alkali silicates.

It is understood that alkali silicates were produced by the ancient Egyptians some 6000 years ago, where sodium (and possibly also potassium) silicates were produced by fusing together quartz sand and naturally occurring soda ash or possibly potash produced from combustion processes.

It is believed that alkali silicates formed an important part of the frescos or wall paintings found in the ruins of Pompeii and Herculanium which were preserved by the eruption of Vesuvius in 79 AD.

The first description of the solubility in water of a fused mixture of flint pebbles with potash was made by Jean Baptiste van Helmont (1577 – 1644), a Brussels physician in his posthumous work "Ortus medicinae", Amsterdam 1648. Independently, Johann Rudolph Glauber (1604 – 1670) obtained a "thick" solution, which he named "Liquor Silicum" from a fused mixture of sand, flint pebbles, or crystalline quartz with potash. Glauber recommended its use as a curative agent, for the production of liquid fluxes in metal smelting, and for glazing earthenware vessels (Furni Novi Philosophici, Amsterdam 1648 – 1650). Even the famous German poet, Johann Wolfgang von Goethe became interested in potassium silicate in 1768, during the course of his alchemical studies.

Despite a number of references in the literature, the commencement of water-soluble silicates being put to practical use occurs at about 1825 when Johann Nepomuk von Fuchs "Professor of Mineralogy and Academician" of Munich, who lived from 1774 to 1856 carried out his pioneering work and investigated the industrial production of water-soluble potassium and sodium silicates, which he named "waterglasses" (i.e., water-soluble glasses) He proposed their solutions could be used as adhesives, cements, fire-proof paints, for sealing porous stone, and as binders for fresco painting. He also coined the name "stereochromie" which was a technique of painting with silicate solutions which he studied extensively. He observed the reactions of silicate solutions with various pigments, and sought to explain in chemical terms such phenomena as precipitation by alcohol, the efflorescence of sodium carbonate from a silicate solution which contained potash as its major base, and the preparation of solutions with a high silica ratio by dissolving hydrous precipitated silica in silicate solutions obtained by dissolving the glassy melts made in the furnace. He proposed silicates as cleansing agents in the laundry directly and in admixture with soap, as reagents in textile dyeing, for fluxes in soldering and welding, and as fertilizers. By 1855 the year before von Fuchs died, water glass was being made commercially both in Europe and in America.

Meanwhile in Europe, on July 23, 1896, in the last days of the industrial revolution at the end of the 19th century, Eduard Woellner laid the foundations for the Woellner Group. At that time, his company, Woellner Werke in Ludwigshafen, produced a number of products, particularly waterglass, washing soda (hydrated sodium carbonate) and Glauber Salt (hydrated sodium sulfate).

Without dwelling any further on the historical aspects of waterborne alkali silicates, let us now move on to more present-day themes.

3. The Woellner Group

Today, the Woellner Group is a medium sized group (by European standards) and is primarily involved in the following three business areas:

- Alkali silicates and special chemicals
- Cosmetics
- Writing inks

Over the past few years it has grown significantly, and now has four manufacturing sites for waterborne alkali silicates in Europe, these are located at:

- Ludwigshafen and Bad Köstritz (Germany)
- Graz (Austria)
- Nogent l'Artaud (France)

The Woellner GmbH & Co. KG, with its own research and development department, produces alkali silicates and special chemicals. Its products are used in the building chemistry, paint and plaster, and paper industries, among others.

Its range of alkali silicates and related products include:

- Lithium Silicates, marketed as Woellner Betolin™ Li series
- Potassium Silicates, marketed as Woellner Betolin™ K and P series
- Sodium Silicates, marketed as Woellner Betol™ series
- Aqueous Silica Sols., marketed as Woellner Betol™ series
- Shotcrete Accelerators., marketed as Woellner Betol™ series
- Silicate Powder, marketed as Woellner Sikalon™ series

Woellner GmbH & Co. KG have more than 100 years of experience with alkali silicates and over 30 years of intense, application-oriented research in the silicate paint and plaster sector. It has particularly focused on the area of the supply of alkali silicates for use in coatings applications such as silicate emulsion paints and plasters, and is probably the best known company in this area in Europe, and has supplied a significant amount of background for this paper

Woellner GmbH & Co. KG design, make and market a range of binders and additives for use in the Betolin System but can also, upon request, offer full support in selecting the appropriate raw materials, formulating finished products and dealing with any questions regarding application.

These additives are classified as:

- Dispersants, marketed as Woellner Sapetin™ series
- Hardeners, marketed as Woellner Betolin™ HT series
- Protective Agents, marketed as Woellner Betolin™ series
- Rheological Additives, marketed as Woellner Betolin™ series
- Stabilizers, marketed as Woellner Betolin™ Q series
- Wetting Agents, marketed as Woellner Sapetin™ series

4. Alkali metals

Firstly, looking at the Periodic Table of the Elements, the Alkali Metals are the Group 1A elements on the left hand side of the Periodic Table shown below and are:

- Lithium (Li)
- Sodium (Na)
- Potassium (K)
- Rubidium (Rb)
- Caesium (Cs)
- Francium (Fr)

Only the first three are of commercial significance for our discussion.

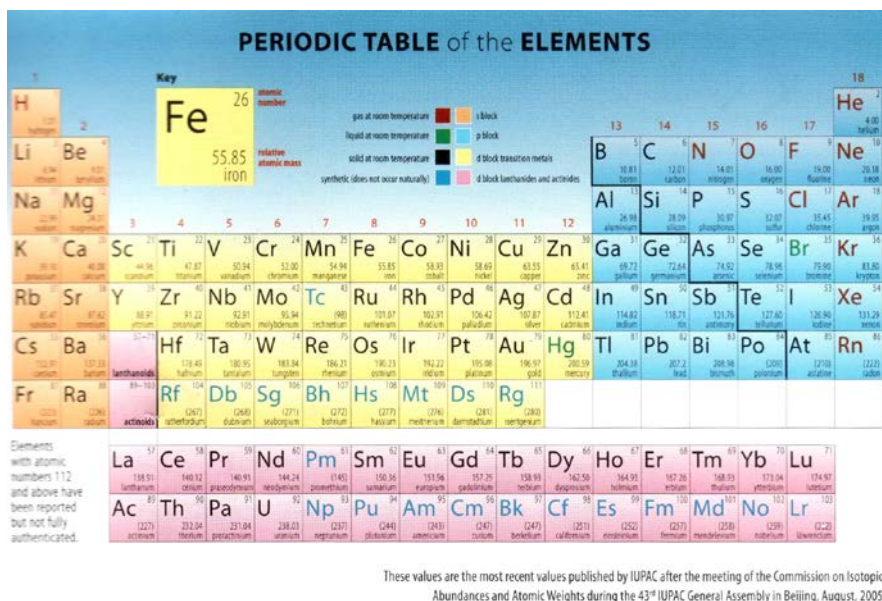
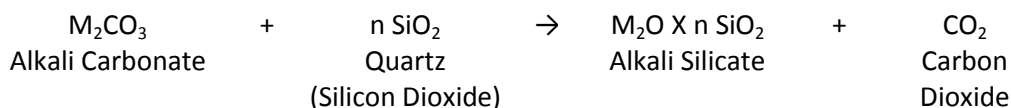


Figure 1

5. Production of alkali silicates

As a starting point, it is worth commenting that to the best of my understanding, alkali silicates represent the only inorganic materials which are frequently used as binders in the coatings industry. Waterborne alkali silicates are entirely synthetic materials, generally of indefinite composition, manufactured by melting sand with sodium or potassium carbonate in glass-making furnaces at temperatures of above 1300°C, and the reaction is represented as follows, where M = sodium (Na) or potassium (K):



Equation 1

The molten glass is run from the furnace onto cooling conveyor belts, and the resulting soluble glass is dissolved in hot water under pressure where any insoluble glass and unreacted sand filtered off. These are true glasses where they do not have any distinct stoichiometric constitution, but rather that the constitution depends upon the ratio of the raw materials in the above equation. The soluble silicates form clear or opalescent colloidal solutions in water which exhibit non-Newtonian viscosity behaviour at all but the lowest concentrations.

The factor n, shown in Equation 1 above is the ratio of silica to alkali-metal oxide, and is called the molar ratio (sometimes designated as R_M). Generally, the usual ratio referred to in common practical use is the weight (wt %) ratio (sometimes designated as modulus, R_W). However, the molar ratio, R_M, can be more useful, particularly when comparing ratios of lithium, sodium and potassium silicates. The conversion factors R_M/R_W are shown below:

Alkali Silicate	Chemical composition	Conversion factor Molar Ratio/ Weight Ratio (R _M /R _W)
lithium silicate	Li ₂ O X n SiO ₂	0.497
sodium silicate	Na ₂ O X n SiO ₂	1.031
potassium silicate	K ₂ O X n SiO ₂	1.568

Table 1

Normal glasses which contain calcium, magnesium, and aluminium silicates are insoluble in water, whereas glasses which contain sodium (Na⁺), potassium (K⁺), can be dissolved in hot water to produce alkaline solutions of various viscosities.

The change in viscosity for weight ratio, R_w for the range of sodium silicates is shown below:

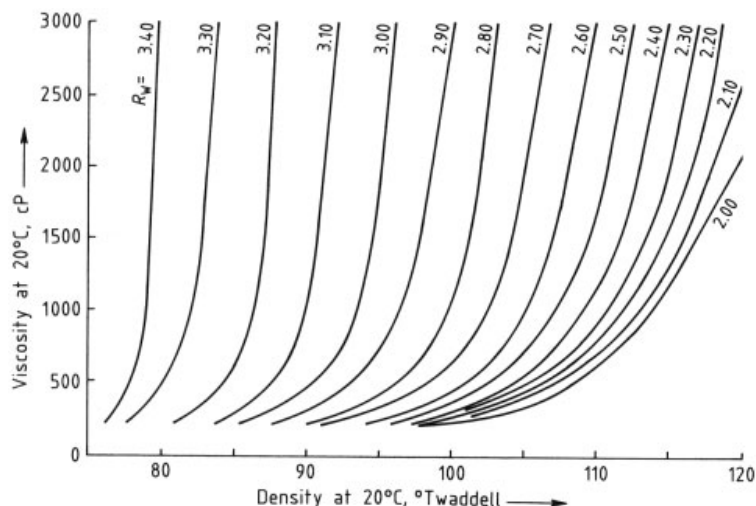


Figure 2

In some countries, different expressions of density are used for alkali silicate solutions. Thus, Twaddell was an arbitrary hydrometer scale used in England during the 19th to 20th centuries, and was derived as follows:

$$^{\circ}\text{Twaddell} = \frac{200 (\text{density of liquid at } 60^{\circ}\text{F})}{\text{density of distilled water liquid at } 60^{\circ}\text{F}} - 1$$

Nowadays, it would be more routinely stated as:

$$^{\circ}\text{Twaddell} = 200 (\text{specific gravity of liquid}) - 1$$

Another scale, sometimes used for alkali silicate solutions is the Baumé Scale, which was derived in France to correlate to the percentage concentrate of a brine solution. Now, considering for liquids heavier than water (which applies to alkali silicate solutions) at a temperature of 20°C, it would be stated as:

$$\text{specific gravity of liquid} = \frac{145}{145 - ^{\circ}\text{Baumé}}$$

Finally to conclude this area of liquid density scales, below is shown the relationship between density, °Baumé and °Twaddell scales.

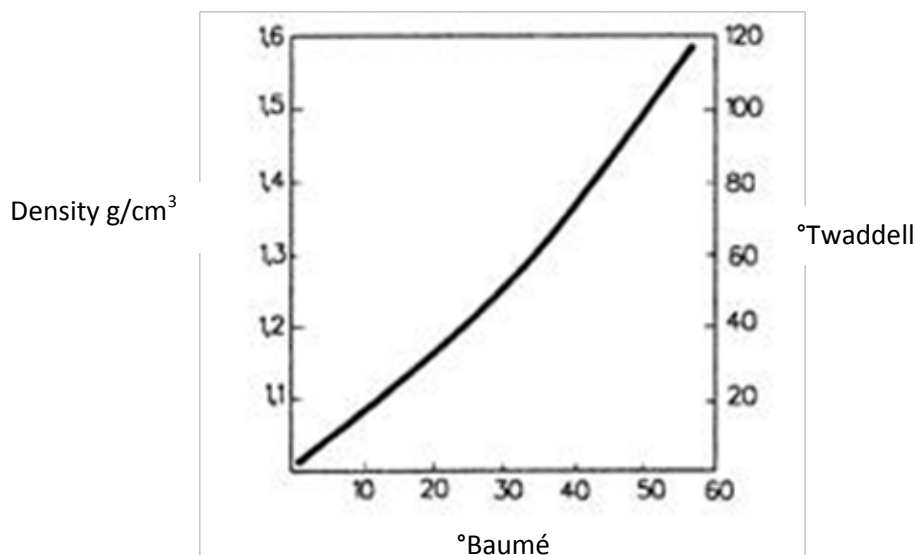


Figure 3

The change in viscosity for weight ratio, R_w for the range of potassium silicates is shown below:

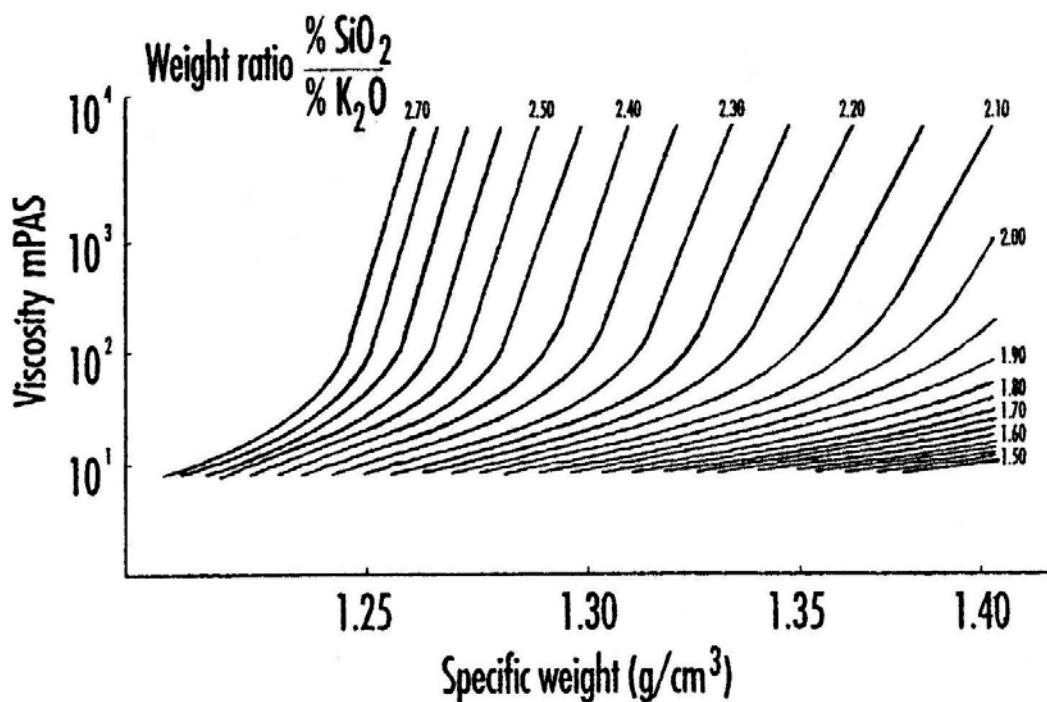


Figure 4

It can thus be seen that commercial alkali silicates are characterized by their solids content and the weight ratio R_w SiO_2 : M_2O (where M is the alkali), which results in certain densities and viscosities.

The correlation between the alkalinity, expressed by increasing pH values, against concentration of alkali silicate for different weight (or molar) ratios is shown below:

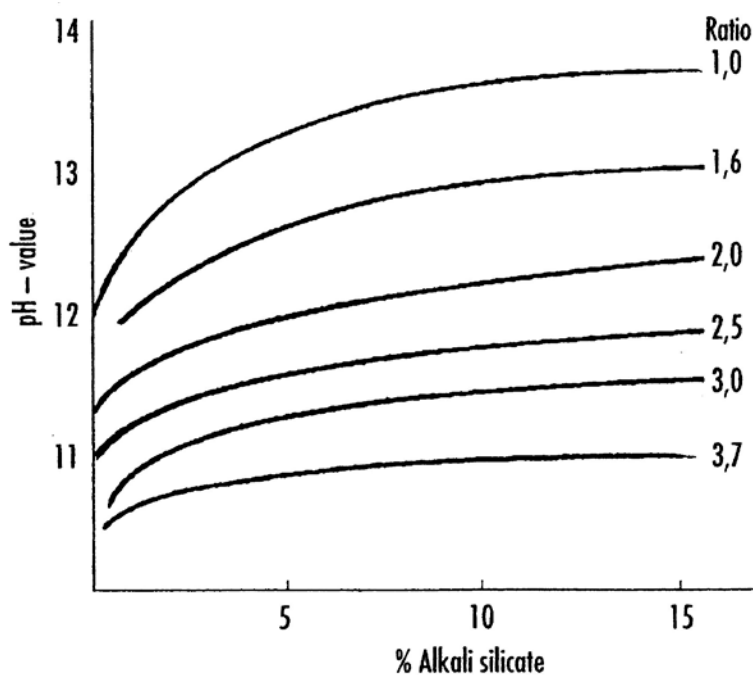


Figure 5

It should be pointed out that pure caustic soda and caustic potash solutions exhibit linear pH curves which lie above the soluble silicate curves.

The correlation between the molar ratio and alkalinity, expressed by increasing pH values is shown below:

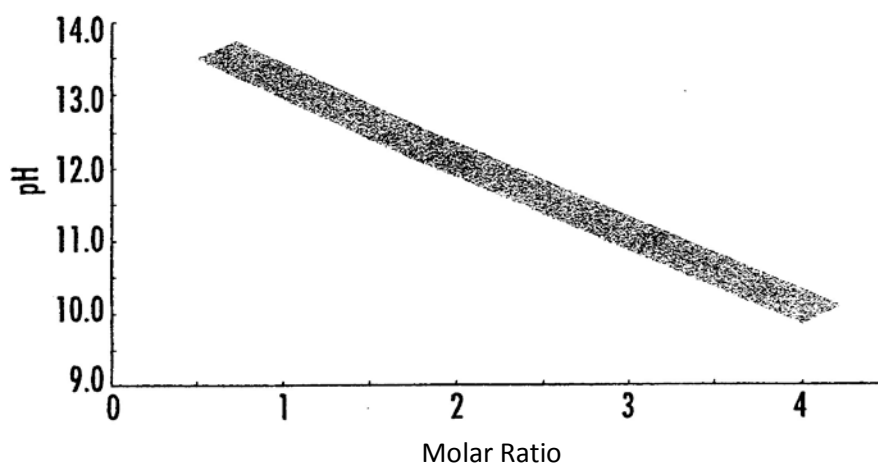


Figure 6

6. Molecular structures of waterborne alkali silicates.

As discussed above, waterborne alkali silicates are glasses which contain a wide variety of species. Using different physicochemical methods in examination of waterborne alkali silicates, the structures of various molecular species have been identified as anions which are monomers, dimers, trimers, tetramers, as well as branched chains, ring structures and 3-dimensional networks.

These structures are shown in Figures 7 and 8 below:

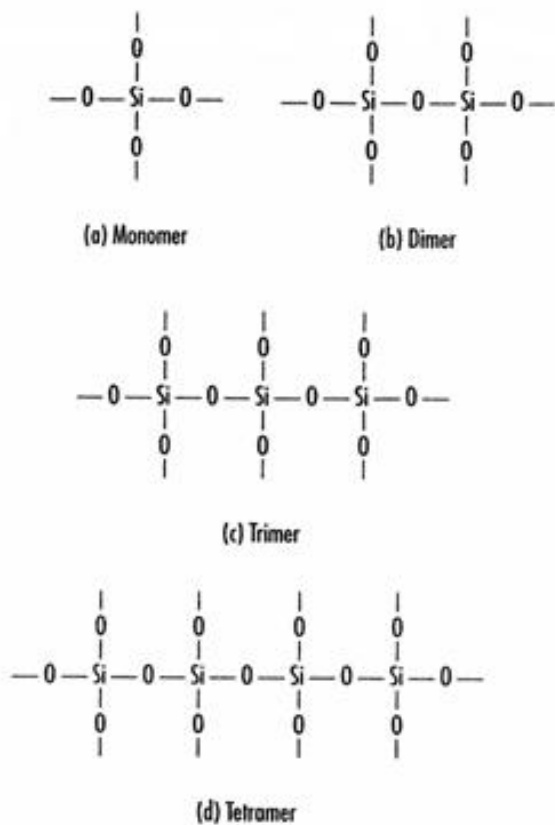


Figure 7

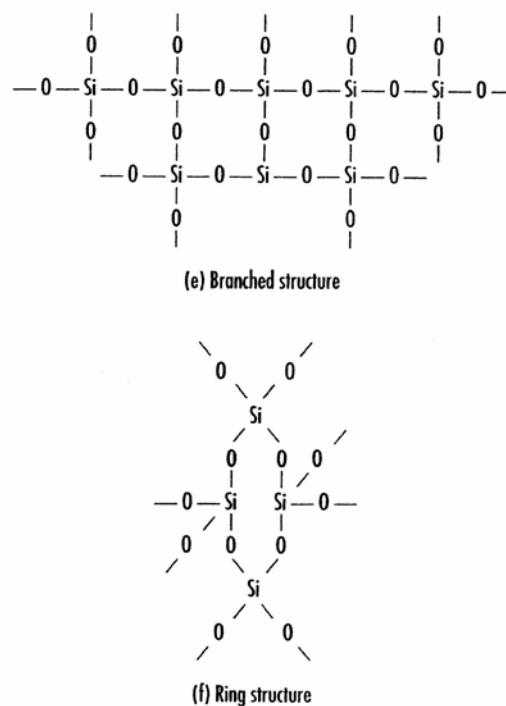


Figure 8

Another way of viewing the silicate structures is shown in Figure 9 below.

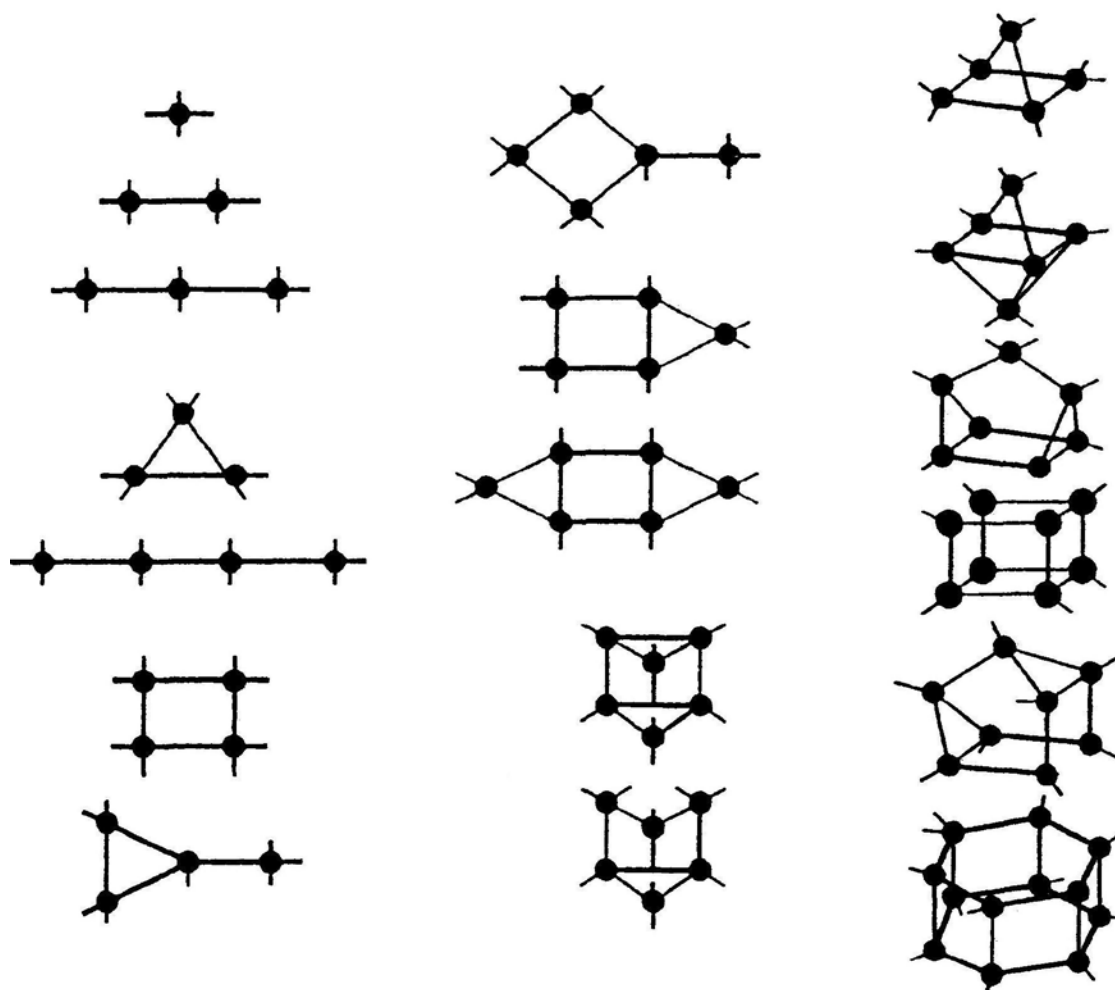
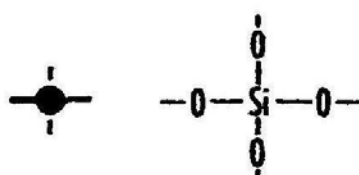


Figure 9

The repeating unit represents the tetrahedral Silicate group:



At varying alkali content levels, the oxygen atoms are present either as undissociated silanol (Si-OH) groups or as negatively charged anions (Si-O⁻), with the counterion being the positively charged alkali cation (M⁺). Dependent on concentration, alkalinity etc the distribution of monomeric, oligomeric and polymeric silicate groups in a solution is not fixed but is in dynamic equilibrium

There are two principal equilibria in the solution, these are:

The acid-base equilibrium:



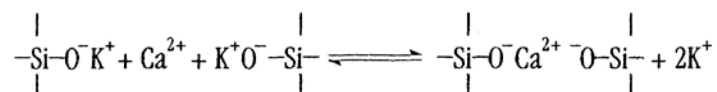
Equation 2

The condensation polymerization or dissociation depolymerisation equilibrium:



Equation 3

Also there is the normally irreversible reaction with polyvalent cations such as Ca^{2+}



Equation 4

The above 3 reactions influence the physicochemical behaviour of silicate aqueous systems in addition to the curing mechanisms on application.

7. Ratio of Silica to Alkali Oxide.

The higher weight (or molar) alkali silicates (which contain relatively lower concentrations of alkali oxide, and in turn proportionately higher concentrations of silica) have understandably lower alkalinity and tend to be the main products used in coating applications. In fact, the ratio of silica to alkali oxide has a significant effect on the coating characteristics, as is shown in the table below:

Effects of different ratios	
The higher the ratio gives the higher:	The lower the ratio gives the higher:
Viscosity	specific weight
drying speed	solubility
curing speed	pH value
susceptibility to low temperatures	susceptibility to water influence
chemical resistance of coatings	tacking and binding power

Table 2

8. Sodium silicates.

So far, we have been looking at the alkali silicates in order of increasing atomic number (i.e. lithium, sodium, and potassium). However in terms of general commercial importance by far the most important alkali silicates which are used in a wide variety of applications are the sodium silicates. Because they represent the greatest majority of alkali silicates manufactured, they are generally the most economic in production cost and selling price and tend to be the most used wherever possible. It has been suggested that some sodium silicates with particular molar ratios are suitable for coating purposes, and on first considering this it might be surprising that sodium silicates are not more commonly used in coating applications.

As we shall see later when we look at the curing of alkali silicates, as a consequence of these reactions in a number of cases alkali carbonates are produced. Sodium carbonate exists in a number of forms with degrees of hydration (water of crystallization) as shown in the following table:

Degree of hydration	Other names	Molecular Formula	Solubility in Water ⁽¹⁾ (g/100 g)
Anhydrous	Soda Ash	Na_2CO_3	30.7 @ 25°C
Monohydrate	Crystal carbonate; Thermonatrite	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	30.7 @ 25°C
Decahydrate	Washing Soda; Natron; Natrite	$\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$	30.7 @ 25°C

Note:

- (1) Solubility in water is expressed as the grams of Sodium Carbonate (excluding water of hydration) which dissolve in 100 grams of water at 25°C.

Table 3

As can be seen from the above table these carbonates existing in various degrees of hydration. The anhydrous product is hygroscopic to absorb water to form the decahydrate which tends to recrystallize to form a white efflorescence on the surface of the cured silicate coating. At the same time sodium silicate paints are mainly post-curing in nature and either require stoving at 175°C or the use of a suitable catalyst to assist room temperature curing. In particular, this concern with efflorescence generally precludes the use of sodium silicate in most coating applications.

9. Potassium silicates.

In common with its sodium analogue, potassium carbonate exists in at least two forms with degrees of hydration (water of crystallization) as shown in the following table:

Degree of hydration	Other names	Molecular Formula	Solubility in Water ⁽¹⁾ (g/100 g)
Anhydrous	Potash	K ₂ CO ₃	111 @ 25°C
Sesquihydrate		2K ₂ CO ₃ .3H ₂ O	111 @ 25°C

Note:

- (1) Solubility in water is expressed as the grams of Potassium Carbonate (excluding water of hydration) which dissolve in 100 grams of water at 25°C.

Table 4

However, as can be seen from the above table these potassium carbonates are not so water rich as the sodium carbonates. The anhydrous product is hygroscopic to absorb water to form the sesquihydrate, which is not hygroscopic, with a much lower tendency to crystallize, and generally does not produce white efflorescence because small amounts of potassium carbonate formed at the surface are relatively easily removed by rain when used particularly on exterior coating applications. At the same time coatings based on potassium silicates are self curing and do not require the use of any added curing agent. However, when used as sole binders without any modification they tend to be relatively slow curing and can be susceptible to leaching out from the coating during the first 24 hours or so. One of the ways to overcome this has been the use of "High Ratio" potassium silicates, with molar ratios of SiO₂:K₂O of 4.8:1 to 5.3:1, and there is an interesting NASA patent (now expired) which refers to the use of such "High Ratio" potassium silicates in 2-K inorganic zinc silicate coatings for anticorrosion protection coatings.

Because of this lack of efflorescence discussed above, we tend to see a significant use of potassium silicates in coating applications whether as 1-K silicate emulsion coatings or as 2-K inorganic silicate coatings.

10. Lithium silicates.

In contrast with its sodium and potassium analogues, lithium carbonate only exists as the anhydrous form with relatively low water solubility (which decreases with rising temperature), as shown in the following table:

Degree of hydration	Molecular Formula	Solubility in Water ⁽¹⁾ (g/100 g)
Anhydrous	Li ₂ CO ₃	1.30 @ 25°C

Note:

- (1) Solubility in water is expressed as the grams of Lithium Carbonate (excluding water of hydration) which dissolve in 100 grams of water at 25°C.

Table 5

Because lithium silicates have high molar ratios (i.e. they have a low alkali content) as well as the consequential lithium carbonate having such a low water solubility, lithium silicate finds uses in applications where the production of water-soluble by-products or any form of efflorescence is undesirable, including 2-K inorganic zinc silicate coatings as well as the strengthening or consolidation of masonry such as natural stone or concrete.

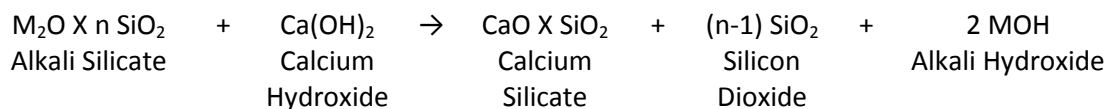
It should be pointed out that lithium silicates are stable at and around room temperature, but precipitate on heating to >ca. 60°C. This effect is reversible upon cooling. Thus, they should not be used in heat accelerated systems.

11. Chemistry of cure of alkali silicates.

The curing process of alkali silicates can involve a number of various basic reactions either with the constituents of the substrate or with the components of air. These can be summarised as below:

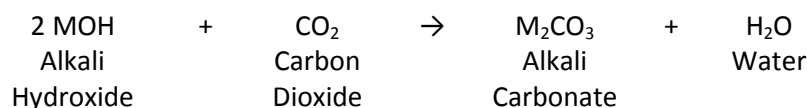
Chemical curing caused by reaction with the constituents of the substrate:

Reaction with burnt lime (calcium hydroxide), where M = sodium (Na), potassium (K) or lithium (Li), as follows:



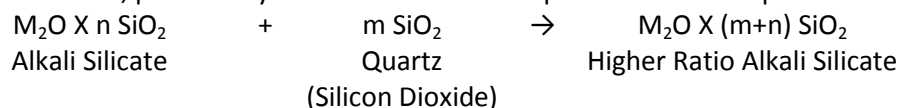
Equation 5

The alkali hydroxide can then react further with atmospheric carbon dioxide to produce alkali carbonate:



Equation 6

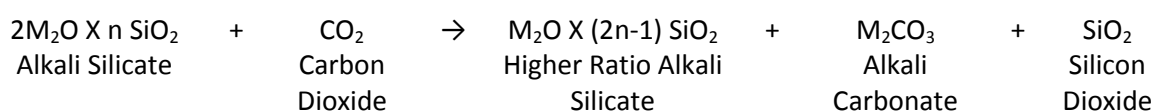
The curing reaction with quartz sand, particularly on the surfaces of the particles can be represented as follows:



Equation 7

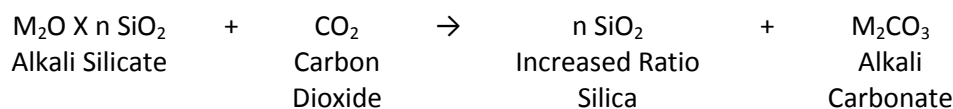
Chemical curing caused by reaction with carbon dioxide from the air:

The chemical curing with carbon dioxide from the air can be represented as follows:



Equation 8

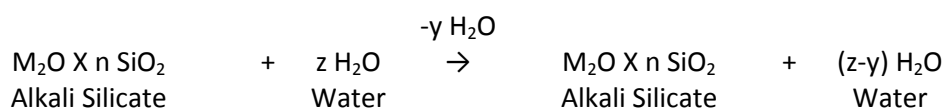
Incomplete silicification can occur with raising of the weight ratio (leading to higher viscosity), which can be represented as follows:



Equation 9

Observant readers will recognize that this is essentially the reverse of the reaction used to manufacture the alkali silicates in the first place from quartz and alkali carbonate.

Complete silicification results in insoluble silica gel formation, with physical water elimination by drying or freezing, can be represented as follows:



Equation 10

As a consequence of this, the higher concentration leads to higher viscosity which leads to gelling.

Incidentally, through the use of certain additives, this process can be produced on demand so that we can effectively accelerate the gelling process, if required.

As we can see from the above equations the inorganic alkali silicate binder systems can be cured in a variety of ways. In essence, the desired curing may be brought about by atmospheric carbon dioxide or by reactive constituents contained in the substrate.

At the same time hardening of the coating may occur by physical water elimination, which may occur by water abstraction through heating or freezing. However in such situations this may only be apparent hardening, such that when further contact with water occurs the coating may soften with the possibility of binder migration.

With properly applied and cured silicate coatings the physico-chemical bond between the binder system and the substrate can be very strong, such that these types of coatings are not regarded as film forming coatings but rather as coatings which essentially become the substrate. At the same time this cured binder produces a porous inorganic substrate with very high water vapour (and carbon dioxide) permeability. Such coatings can be of advantage particularly on historic buildings, (which can often be damp) as well as coatings on incompletely cured concrete. In the case of damp historic buildings, the passage of water vapour permits damp buildings to effectively dry out. For coatings on incompletely cured concrete, the passage of carbon dioxide is permitted to occur thus leading to subsequent carbonation (with consequent hardening of the concrete). Generally film forming coatings based on e.g. pure organic emulsion paints, although considered to be permeable, still hinder the passage of water vapour through the substrate, and have nowhere near as high a gas permeability as coatings based on silicates. With the above background in the chemistry of curing of alkali silicates in mind, we now move on to the area of applications of these products.

12. Applications of alkali silicates.

The range of applications of alkali silicates is very wide, including adhesives, detergents etc, but for this discussion we are concentrating on coatings and related areas.

12.1. Coatings

In the coatings area we will cover applications for the 2-K silicates and the 1-K silicates.

12.1.1. Applications of alkali silicates in pure silicate coatings (2-K silicates).

Here we can consider architectural coatings and inorganic zinc silicate coatings.

12.1.1.1. Applications of alkali silicates in pure silicate architectural coatings (2-K silicates).

As discussed earlier, a number of workers experimented with alkali silicates and in 1879 Adolf Keim of Augsburg in Bavaria was granted German patent number 4315 for silicate-based mineral wall paints, as shown in Figure 10.



Figure 10

To this day, the company known as Keim Farbe still bears his name, and is one of the best known companies worldwide involved in manufacturing and supplying of mineral-based paints.

Such coatings have the following advantages:

- Silicate based masonry paints are suitable for indoor and outdoor applications.
- They can be supplied at an acceptable cost level.
- Their adhesion on to the siliceous masonry substrate is very high because of the chemical reactions between the binder and the masonry substrate.
- Silicate based masonry paints have excellent resistance to industrial gaseous pollutants.
- Silicate based masonry paints can provide the most superior exposure durability to weathering of all coatings.

A typical starting point formula is shown in the table below:

Ingredient	Mass
<u>Component A (Powder)</u>	
Marble filler with optimal storage	30.0
Silicate earth	20.0
Thickening agent	0.2
Titanium dioxide	3.0
Zinc oxide pigment	11.5
Lithopone	6.0
Quartz	10.0
Marble filler	9.1
Barium sulfate	10.0
<u>Sub-total Component A</u>	99.8
<u>Component B (Liquid)</u>	
Potassium silicate (e.g. Woellner Betolin™ type)	71.3
Water	28.4
Glycerine	0.3
<u>Sub-total Component B</u>	100.0

Table 6

The procedure is to mix Components A and B in a 3:1 ratio and allow to mature before application.

So if these coatings are so durable why are they not used more often nowadays? As can be seen from the formulation this is a 2-component (often referred to as 2-K) coating. It requires mixing on site, and needs to be left to ripen or mature for some time before they can be used on the substrate.

Also it would appear that these paints are unable to cure when the relative humidity drops below 20%. Whilst on the face of it, it would appear that this restriction of low relative humidity could be a barrier against the use of these coatings (and possibly also the 2-K zinc silicate coatings discussed in the next section), further examination suggest that this may not be such a concern. Australian Bureau of Meteorology data collected over a 30 year period (from 1961 to 1990) suggests that conditions of relative humidity below 20% only typically occur in the afternoon in isolated locations such as Marble Bar and the Western Desert usually during the months around October. Looking at the Australian Bureau of Meteorology data, no Australian capital cities show relative humidity below 20% at any time during the year.


2-K coatings are still used nowadays, but apparently only in relatively special situations, and even then predominately by Master Painters who with appropriate care and attention can accommodate their disadvantages in mixing and application. The mechanism of cure of such coatings would be expected to follow the equations discussed in the earlier section on Chemistry of Cure.

11.1.1.2. Applications of alkali silicates in inorganic zinc silicate coatings (2-K silicates).

Here it would be remiss to ignore the pioneering work carried out by Victor Nightingall, who essentially started the industry of inorganic zinc coatings in Melbourne during the 1940s. There is an excellent publication available from the Australasian Corrosion Association Inc, which reviews 60 years of this industry and it is recommended to any who are interested in this topic, although they are becoming scarcer daily! What I find of great personal interest in this topic is the fact that the industry started by Victor Nightingall has now become a worldwide industry, and yet outside of those involved in the specialised area of Anti-Corrosion Protective Coatings I am not sure that his contribution to the paint industry is well recognized. In fairness to the Australasian Corrosion Association, since 1997 (50 years after his passing) they have made an annual award known as the "Victor Nightingall Award" to honour a coatings specialist who has made an outstanding contribution to the protective coatings industry in Australia and New Zealand. A number of recipients of this award are and have been members of our association.

Victor Nightingall's formal training was in the area of electrical engineering, (where he gained his only academic qualification), although he later carried out further studies in chemistry and chemical engineering. Possibly his first area of training encouraged him to look at the area of the prevention of corrosion, where he was most successful, despite carrying out other work in other relatively unrelated technical areas.

In the area of anticorrosion protection, he recognized the potential of silicate based coatings loaded with high levels of zinc. The silicate binders on which he carried out his work initially were the sodium silicates, presumably on the basis of cost and availability. The original product (referred to in Australian patent number 104,231, lodged in 1937, with the title of "Improvements in and connected with silicated compositions" and shown below) was composed of zinc dust which was mixed on site with a solution of sodium silicate to which a small amount of sodium carbonate (to produce carbon dioxide on heating to a temperature of nearly 100°C), and sometimes other pigments were incorporated. The cross linking and polymerization of the silicate ions formed polysilicic acid, and this silicate matrix reacted with the zinc to form a silica zinc polymer. Such coatings were formulated to be typically applied onto steel surfaces such that the reaction which occurs between the steel, zinc particles and the silicate binder produced a complex chemical structure which effectively becomes part of the steel surface. Over the ensuing life of the coating further reactions occur with any residual alkaline silicate being neutralized (particularly by reaction with atmospheric carbon dioxide) producing a dense metal like coating. Even zinc corrosion products which may be formed assist in filling the pores of the coating. Although other zinc rich coatings such as e.g. 2-K zinc rich epoxy coatings have also gained significant usage, it appears that inorganic zinc rich coatings can improve in durability with age in contrast with organic coatings.



Department of Patents
Trade Marks and Copyrights
Commonwealth of Australia

104,231

Application Date: 20th Mar., 1937 No. 1117/37

Applicant (Actual Inventor) VICTOR CHARLES JOHN NIGHTINGALL.
 Application and Provisional Specification .. Accepted, 13th April, 1937.
 Complete Specification after Provisional Specification .. Lodged, 17th July, 1937.
 Complete Specification Accepted, 14th June, 1938.
 Acceptance Advertised (Sec. 50) 30th June, 1938.

Classes 79.3; 18.5

No drawing

COMPLETE SPECIFICATION.

"Improvements in and connected with silicated compositions."

I, VICTOR CHARLES JOHN NIGHTINGALL, Consulting Engineer, of 79 Mount Street, Heidelberg, in the State of Victoria, Commonwealth of Australia, hereby declare 5 this invention and the manner in which it is to be performed, to be fully described and ascertained in and by the following statement:-

This invention relates to improvements 10 in and connected with silicated compositions and refers especially, but is not limited, to the formation of protective coatings from materials containing soluble silicates and finely divided metals (particularly zinc) 15 such coatings being applicable to the surfaces of metal, glass, concrete and other materials.

The invention also comprehends the formation of articles of manufacture from 20 materials of the same general character.

It has been previously proposed to employ mixtures containing soluble silicates and finely divided metals as cements, paints and the like.

It has also been proposed to form protective and like coatings on metals by applying thereto a mixture containing water glass and finely divided aluminium or magnesium or alloys thereof, such coatings being alloyed 5 to the base metal by a subsequent heat treatment.

Now, the object of the present invention is to provide improvements in the formation of coatings and moulded bodies from mixtures containing silicates and finely divided 10 metals and/or compounds thereof.

The invention broadly resides in forming a coating by applying an aqueous solution of silicate and a finely divided metal or 15 metals and/or compounds thereof to a surface and converting the mixture to a substantially insoluble condition in the presence of carbon dioxide.

For this purpose the coated article may be 20 heated in an atmosphere of CO₂ to facilitate the conversion of the coating to a substantially insoluble condition.

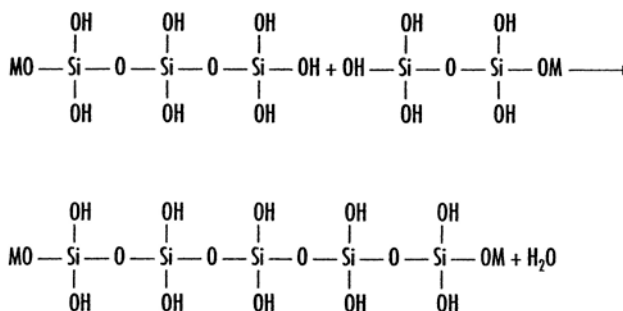
Figure 11

As a postscript to the story of Victor Nightingall, the company which he was involved in founding was called Dimet Pty Ltd. In 1974 it was sold to PGH Industries, and after being owned by a number of companies it was acquired by Jotun of Norway in 1992 with its name disappearing in Australia in 1995. Its name however still lives on in various companies that were founded in a variety of countries, particularly in South-East Asia.

Subsequent developments in inorganic zinc silicate based coatings have focused more on potassium silicate as a binder. Potassium silicate coatings are self curing at ambient temperatures and do not require the addition of any curing catalyst, and on atmospheric exposure, they do not develop white carbonate efflorescent films, unlike those based on sodium silicates.

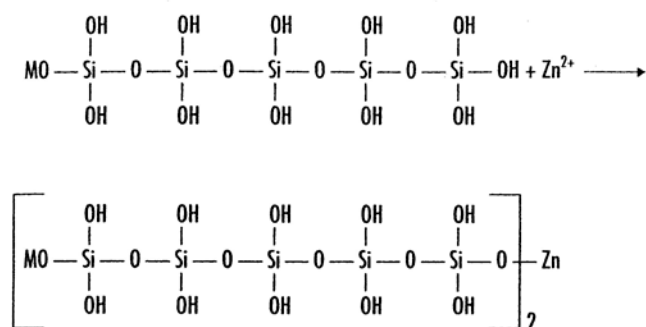
Unfortunately, under conditions of high humidity and low ambient temperature such coatings can cure relatively slowly with a water insolubility ranging from 1 hour to 24 hours or longer. Nevertheless from the early 1960's to the late 1970s such inorganic zinc silicate coatings based on potassium silicate were the most generally used primers. Because in these coatings we are considering alkali silicates being used with a high loading of zinc dust and typically coated onto steel, then we do not expect to see the same types of reactions as we discussed earlier which were primarily on siliceous substrates such as masonry, where the presence of calcium ions is frequently encountered.

Initially, as the water evaporates from the alkali silicate/zinc coating, there is a concentration of binder with initial drying and primary deposition of the coating on the substrate. After evaporation of water, silicate prepolymer is formed as shown in the equation below:



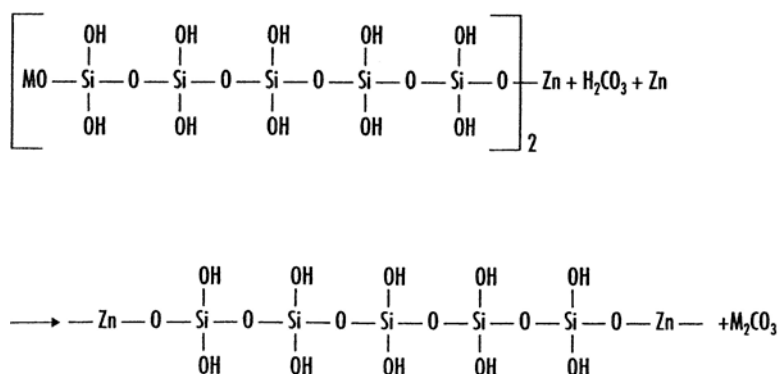
Equation 11

Insolubilization of the silicate matrix by reaction with zinc ions from the surface of the zinc particles, together with possibly ferrous (Fe^{2+}) from the steel substrate to form iron zinc silicate polymer as shown in the equation below:



Equation 12

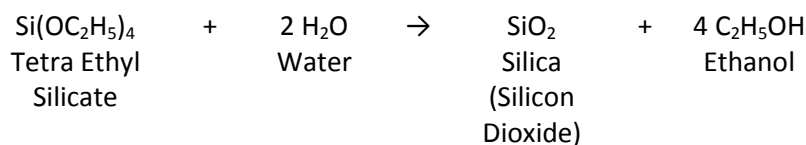
Subsequent to this, the silicate undergoes a hydrolysis reaction in the presence of carbonic acid (present in the atmosphere and formed from carbon dioxide and water) to produce polysilicic acid which then reacts further with the zinc ions present in the zinc dust to form a zinc silicate polymer which gives a 3-dimensional inorganic matrix structure. This final reaction, shown below, which takes many months to complete, is expected to occur at the surface of the coating with the atmosphere, and gradually moves through the depth of the coating down to the steel substrate. Over this period the cross-link density of the coating is increased such that a very hard, durable and dense coating is achieved.



Equation 13

Although this is not a central theme of this presentation, we should just mention that since the late 1970s the dominant binder used has been that of solventborne ethyl silicates, which after air drying for 20 to 30 minutes produce a coating which does not suffer from damage through exposure to early rain.

Essentially the silicate binder produced from the tetra ethyl silicate reacting with water is similar to the silicate binder produced from waterborne alkali silicates, with ethanol being produced as a by-product rather than alkali carbonates, as shown below:



Equation 14

Here we have simplified the situation, by ignoring the formation of the iron zinc silicate polymer as described above. Nevertheless, with the formation of the silica, through production of polysilicic acid, it can be considered to produce a similar zinc silicate polymer giving way to a 3-dimensional inorganic matrix structure essentially similar to that produced using the waterborne alkali silicate.

The above tetra ethyl silicate systems are normally 2-K, in other words one pack normally contains binder while the other contains the other ingredients (generally powder) include pigments. Usually these systems are mixed on-site just prior to applications in accordance with the manufacturer's specification.

It is appropriate to point out that 1-K tetra ethyl zinc rich silicate systems do exist where free water (as opposed to chemically bound water) has been excluded to avoid gassing problems. However whilst these have the attractiveness of not requiring mixing on-site, they are extremely difficult to formulate successfully such that an acceptable shelf life of such a 1-K system is guaranteed. It is believed that such 1-K systems only form a very small proportion of the commercial market.

With the emphasis on environmental acceptability, and reducing the use of solvents in coatings, as well as simplifying cleanup (using water instead of solvent), it is significant to see that one of the major anticorrosion paint manufacturers has recently launched a waterborne inorganic zinc silicate coating for corrosion protection. Other companies appear to have had such products on their product range for a number of years. Possibly there is an increased emphasis on waterborne alkali zinc silicate coatings, which seems to be fulfilling a forecast made a number of years ago that with the changes in environmental requirements of coatings, the emphasis on such coatings was expected to grow in the future. Looking back at the original work carried out by Victor Nightingall, perhaps one might say this is an example of the wheel somewhat turning full circle!

Lithium silicates with a silica ratio of up to 8.5:1 are generally used to formulate waterborne inorganic zinc coatings. They have the advantages of also being self curing at ambient temperatures, having long pot lives and can develop good water resistance within an hour of application. They have the best performance in anticorrosion protection of any waterborne inorganic zinc silicate coating, because they have the lowest alkali content, producing higher binding power and less efflorescence. Also, as discussed earlier, any lithium carbonate that is produced during curing is water insoluble and should therefore not provide any path of weakness of the coating. Cured films are regarded as being similar to those of baked sodium silicate binders and are characterized by great hardness, durability and abrasion resistance. I recall a colleague involved in the protective coatings industry who was involved in the supply of anti-corrosion protective coatings telling me that such coatings were used in the marine industry on decks of ships (as well as on the insides of tanks) where their abrasive resistance would certainly be tested and were found to be superior. A typical starting formulation is supplied as Table 7. Unfortunately lithium silicate is a somewhat more expensive binder than potassium silicate, and on the basis of achieving an appropriate economic level of protection and durability it would appear that blends of potassium and lithium silicates are more commonly used.

Ingredient	Mass
Component A (Powder)	
Zinc dust, ca. 7 μ	75.0
Chromium (III) oxide green	5.0
Muscovite mica MU – M 2/1	18.0
Natural bentonite – NA (Wyoming)	1.0
Woellner Betolin™ V 30, thickener	0.2
Sub-total Component A	99.2
Component B (Liquid)	
Lithium silicate (e.g. Woellner Betolin™ Li 24)	99.4
Dispersant (e.g. Woellner Sapetin™ D 20)	0.4
Alkali stable wetting agent	0.2
Sub-total Component B	100.0

Table 7

The procedure is to mix Components A and B in a 1:1 ratio and mix homogeneously.

12.1.2. Applications of alkali silicates in silicate emulsion coatings and plasters (1-K silicates).

With the experience of long-term stability of exterior coatings based on 2-K silicate paints as well as the benefits of organic emulsion paints with their attractiveness, ease of production and good storage stability, there was a desire for a single pack (1-K) coating system to exhibit the properties of mineral paints together with ease of production, ease of application and good storage stability. Requirements of such a 1-K coating system were to include the following:

- Ready-to-use products
- Easy and fairly quick production
- Proper rheological behaviour
- Stabilization of binder - filler/pigment system against reagglomeration
- Good storage stability (shelf life at least one year)
- Small degree of syneresis and sedimentation
- Good redispersibility on stirring
- Good application properties
- Sufficient diffusion into substrate for strong adhesion and surface hardening
- Reinforcement of substrate
- Good and equal colour retention on the substrate
- Perfect curing without chalking
- Good weathering stability
- Maintenance of easy water vapour permeation

1-K Silicate emulsion systems were created to satisfy these criteria in the areas of paints and plasters.

12.1.2.1. Main constituents of silicate emulsion coatings (1-K silicates).

The main constituents of silicate emulsion paints and plasters are:

- Water
- Inorganic binder (typically potassium silicate such as Betolin™)
- Organic binder (typically styrene acrylic dispersions or other alkali-stable organic dispersions)
- Fillers
- Pigments
- Additives

In order to maintain the essentially inorganic nature of the coating on the masonry substrate (typically a wall) and the water vapour permeability, the total level of organic content must be restricted. The German standard DIN 18 363 which refers to painting and coating defines silicate emulsion paints as those containing no greater than 5% w/w of organic content based on the total mass of formulated product as determined by the loss on ignition at 450°C/2h of a material pre-dried at 200°C/2h.

The formulation of a silicate emulsion paint is an easy process, although it should be pointed out that the individual components can cause complex interactions. Understandably, the choice of raw materials and the process of addition is important for the quality of silicate emulsion paints and plasters.

12.1.2.1.1. Selection of organic polymer emulsion for silicate emulsion coatings (1-K silicates).

A point in question is the selection of the organic polymer emulsion which is suitable for mixing with the potassium silicate. Here a compatibility test is carried out between the potassium silicate and the organic polymer emulsion using the following starting point formula:

Ingredient	Mass
Water	70
Organic polymer emulsion	10
Potassium silicate (e.g. Woellner Betolin™ P35)	20
TOTAL	100

Table 8

The procedure followed is:

1. Dilute organic polymer emulsion with water.
2. Slowly add potassium silicate under stirring.
3. Give the system a little time to defoam (according to requirement, maximum time is approx. 1-2 hours).
4. Pour the mixture over a glass plate and examine the resulting film.
5. The film should be clear without any spots, particles or irregularities.
6. Repeat the test after one week storage of the mixture in an oven at 60°C.

12.1.2.2. Production of silicate emulsion coatings and plasters (1-K silicates).

Normally after preparation, silicate emulsion paints and plasters are permitted to stand for up to a week. During this period the viscosity performs thickening such that the final viscosity is achieved. The nature of the thickener is critical as well as the interaction with the binder, the temperature and choice and purity of raw materials. It is therefore recommended that stock mixtures be prepared and sufficient quantities of these to be kept in store. In particular this applies to textured finishes, because grain size distribution can be obtained for the individual qualities.

The physico-chemical interaction of the components is directed by certain hydration and swelling processes and by:

- forces of repulsion
 - Horn approximation (collision diameter)
 - Coulomb repulsion (electrostatic forces)
 - repulsion by adsorbed polymer particles
- forces of attraction
 - Van der Waals forces (dispersion and induction forces,
 - dipole-dipole orientation)
 - hydrogen bridging bonds
 - electrostatic attraction by interfacial charges
 - formation of polymer bridges

12.1.2.3. The formulation, assessment and production of silicate emulsion paints and plasters.

Typically the formulation components which are involved are as follows:

Binders

- inorganic
 - potassium silicate solutions
 - pre-stabilized potassium silicate solutions (mostly recommended)
- organic
 - polyacrylates
 - styrene acrylates
 - terpolymers

Fillers and Pigments

- Fillers
 - quartz
 - calcite
 - clay
 - talc
 - barytes
 - Neuburg chalk
 - fibrous materials
 - plastorite
 - Na-Al-silicates

- Pigments
 - titanium dioxide
 - lithopone
 - inorganic unreactive pigments (e.g. inert iron oxides, BaSO₄ etc)

Without trying to single out any particular area of concern, the suitable choice of fillers and pigments is very important, and they should not contain any reactive polyvalent cations (Ca²⁺, Mg²⁺, Al³⁺, Fe³⁺), since the presence of these can cause thickening and possibly gelling of formulations. As an example for this reason, the use of dolomite fillers should be avoided.

Additives

Additives which may be used in silicate emulsion systems include:

- Dispersants: polyphosphates, polyacrylates, phosphonates, naphthene and lignin sulfonates
- Wetting agents: anionic, cationic, amphoteric and nonionic surfactants
- Defoamers: silicon emulsions, hydrocarbons, long chain alcohols etc.
- Stabilizers: special polyfunctional, mostly cationic compounds
- Coalescents (if needed): alkali-stable esters, glycols, hydrocarbons
- Rheological additives: cellulose derivatives (CMC, HEC), xanthan gums, polyurethane, polyacrylate, modified starch, bentone and other lamellar silicates
- Water repellents: alkyl siliconates, siloxanes, wax emulsions, fatty acid Li salts
- Biocides: (Generally, due to their alkalinity silicate emulsion paints and plasters do not need special in-can preservatives, but it may be necessary to incorporate special algaecides or fungicides for film preservation).

The pH of the final silicate emulsion paint or plaster is expected to be typically in the area of 10.0-10.5, and so any additives should be resistant to saponification at that level of alkalinity.

Testing formula

As discussed earlier, to screen test for good long term stability of the products (aiming for a shelf life of at least 1-2 years), it is recommended that each raw material be tested in a standard testing formula, as shown in the following example for a silicate emulsion paint. The silicate emulsion paint/plaster is produced according to the standard testing formula, and samples are stored in close containers:

- at room temperature (about 20°C)
- at elevated temperature of say 60°C (for accelerated stress testing)

Ingredient	Mass	Process
Water	17.2	
Dispersing agent(e.g. Woellner Sapetin™ type)	0.2	
Thickening agent	0.2	
Stabilizer (e.g. Woellner Betolin™ Q type)	0.5	dissolve
Titanium dioxide	10.0	
Defoamer	0.2	dissolve
Filler (carbonate type)	30.0	add with stirring
Filler (silicate type)	7.5	
Polymer dispersion	8.0	add and stir for about 10 minutes
Butyl diglycol	0.5	
White spirit	1.0	
Potassium silicate (e.g. Woellner Betolin™ type)	24.6	add and stir to homogeneity
Rheological additive/viscosity regulator (e.g. Woellner Betolin™ type)	0.5	
TOTAL	100.4	

Table 9

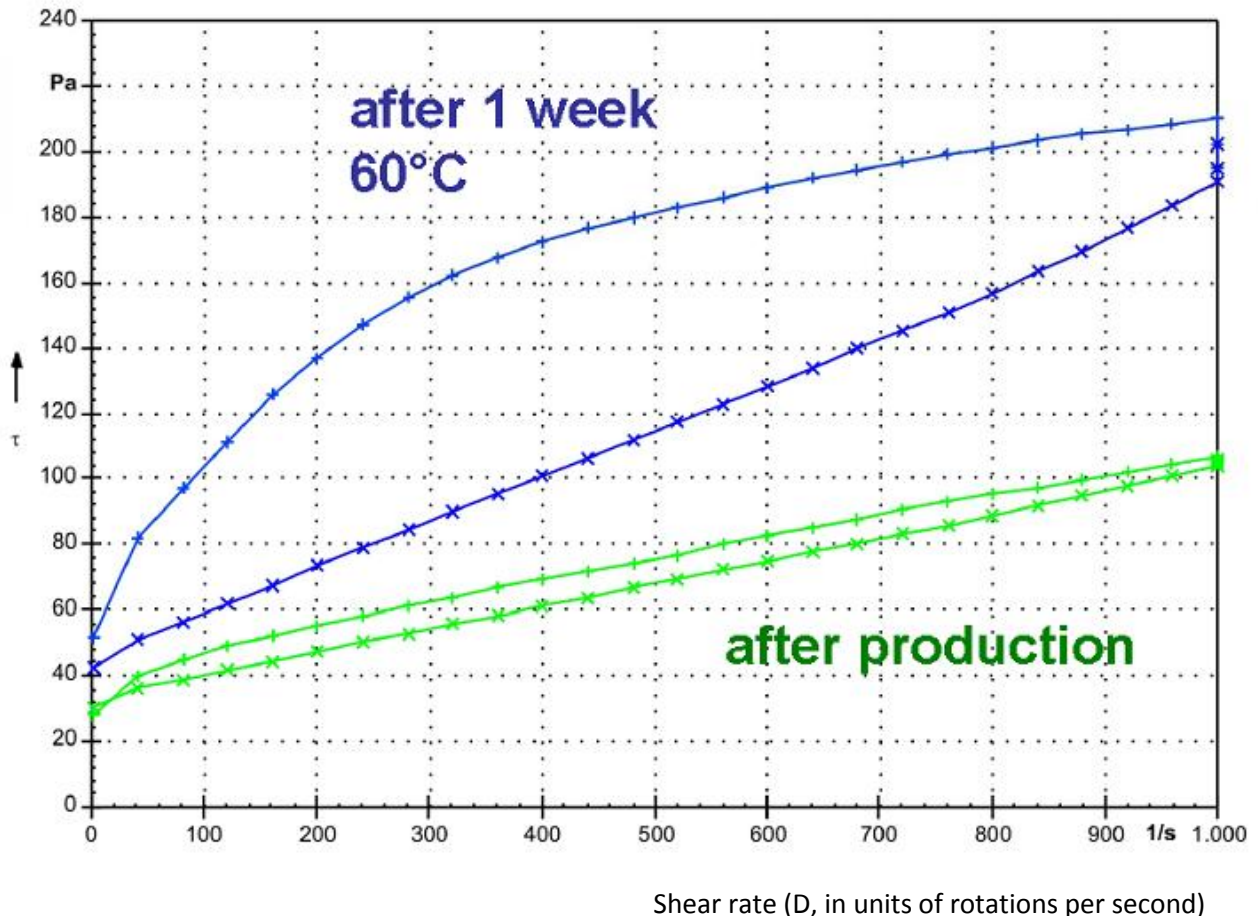
After being stored for one day and then at defined intervals of up to at least 30 days the quality is assessed with regard to the following parameters:

- Silicate emulsion paint/plaster properties, including:
 - Syneresis (water on top of system)
 - Deposition of solids
 - Stirrability
 - Viscosity development
 - Thixotropy
 - Agglomeration or coagulation
- Silicate emulsion paint/plaster application properties, including:
 - Hiding power
 - Wash and scrub resistance
 - Very low chalking

It should be possible to formulate and produce stable products using strictly quality controlled pure potassium silicate solutions, however the use of pre-stabilized potassium silicate products can provide a much easier path to develop a suitable formula with consistent quality over the life of the product.

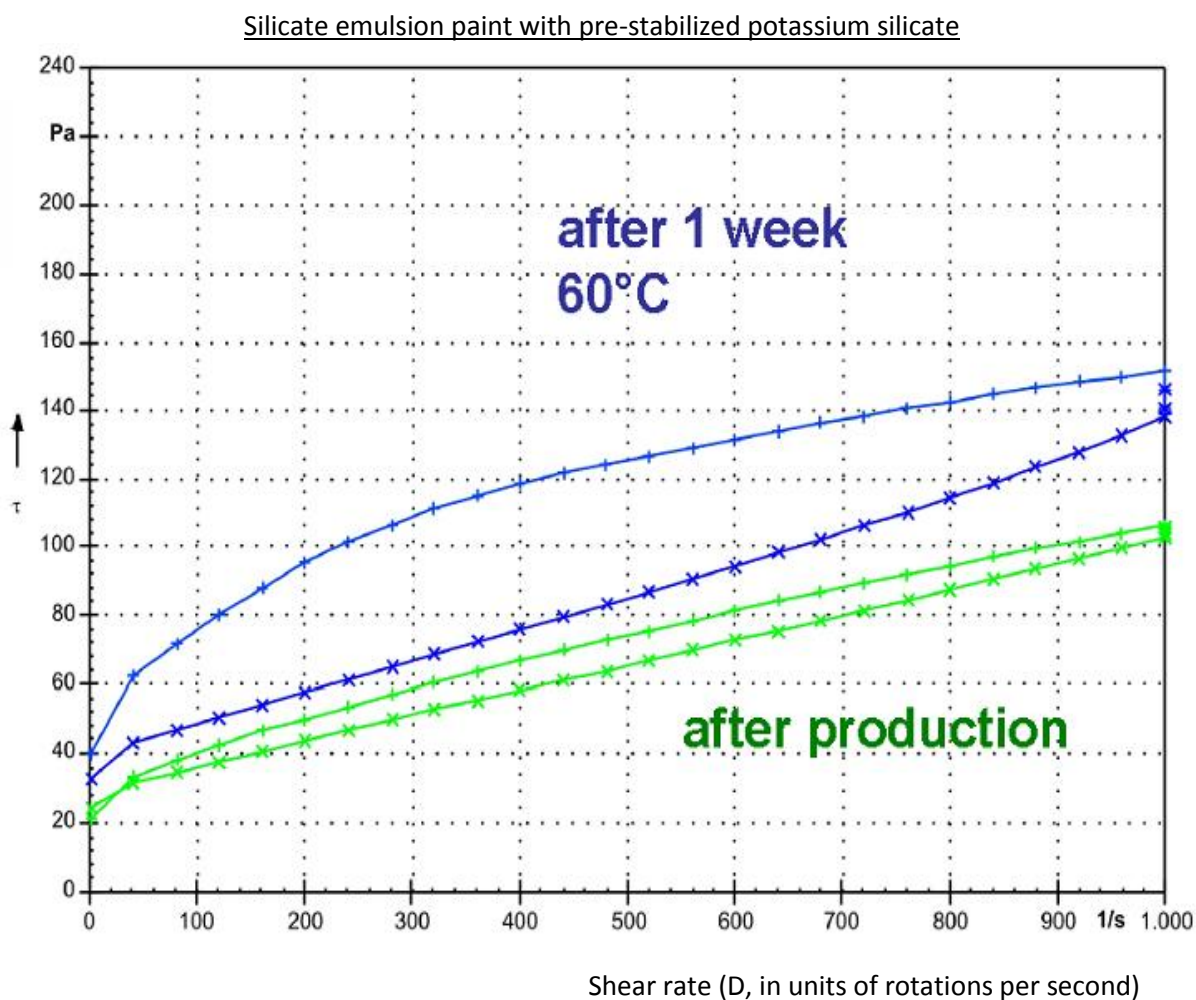
In Figures 12 and 13 below, we can see the different behaviour of silicate emulsion paints based on unstabilized and pre-stabilized potassium silicates in regard to the shear stress (τ , in units of tau/Pa) against shear rate (D, in units of rotations per second). These graphs compare measurements in the upwards curve (signified as + on the graphs) against the downwards curves, (signified as x on the graphs) with the development of thixotropy expressed by the areas under the curves.

Silicate emulsion paint with unstabilized potassium silicate



+ = Upwards curve, x = Downwards curve, Measurement system, Z3 DIN, 02-2001

Figure 12



+ = Upwards curve, x = Downwards curve, Measurement system, Z3 DIN, 02-2001

Figure 13

It is quite apparent, particularly with the testing at 60°C, that there is an undesirably much greater increase in viscosity and development of thixotropy in the silicate emulsion paint based on the unstabilized potassium silicate than with the one based on the pre-stabilized potassium silicate.

Silicate binder contents

The paint in the testing formula described above contained about 6.9% of potassium silicate, based on the use of 24.6 % w/w of 28% w/w solids of potassium silicate solution. We recommend that the effective amount of potassium silicate in the finished formulated product should be as in the following table:

Application	Recommended Potassium Silicate solid content
Exterior paints	Ca 4.5-7.0%
Interior paints	Ca 3.5-5.0%
Plasters	Ca 2.0-4.0%
Brush or spray plasters	Ca 3.0-5.0%
Primers	Ca 5.5-8.5%

Table 10

As the silicate binder content increases, generally the following will be observed:

- Higher viscosity
- Less tendency to thicken on storage
- Significantly larger thixotropy areas
- Slight increase in spreading resistance on application
- Less easy levelling
- Higher tendency of 'burning up', especially on warm and dry substrates
- Slightly higher tendency for white efflorescence
- Higher tendency for colour variation on different substrate surfaces
- Slightly lower water resistance at the beginning of the curing period

Polymer dispersion content

As the organic polymer dispersion content increases, generally the following will be observed:

- Slight increase in viscosity
- Slightly smaller thixotropy areas
- Sometimes less tendency of colour variations on different substrates
- Earlier water resistance

12.1.2.4. The application of silicate emulsion paints on various substrates.

Below, we provide our recommendations regarding the suitability of various substrates for coating with silicate emulsion paints and plasters.

- Silicate emulsion paints can be applied on most mineral and also various other substrates, such as:
 - Fresh or set high calcium lime-sand mortar (interior)
 - Fresh or set lime-cement-sand rendering
 - Fresh or set cement rendering
 - Concrete surfaces (after removal of formwork and release agent residues)
 - Sand-lime-brick masonry
 - Brick masonry
 - Fibre cement (e.g. cellulose fibre cement) boards
 - Metal surfaces, especially aluminium and galvanized iron
- Silicate emulsion paints can be fairly suitably applied (after pretreatment or where necessary with specially formulated products) on:
 - Natural stone (depending also on stone type)
 - Kiln fired brick
 - Aerated cellular concrete (very porous, causing high absorption)
 - Inorganic foamed insulation materials
 - Iron surfaces (e.g. interior fire proofing coatings)
 - Fresh limewash coatings
 - Old limewash coatings
 - Old strongly adherent emulsion paint coatings (water vapour permeation will not be obtained)
- Silicate emulsion paints are unsuitable for application (or only after special pretreatment with specially formulated products) on:
 - Gypsum finish (pretreatment strictly required)
 - Particle boards
 - Existing oil paint coatings
 - Fatty or oily or strongly soiled surfaces
 - Plastic surfaces

All substrate surfaces should be of such condition that good but not unnecessarily high penetration of the paint into the pores and capillaries can be achieved. For example, cement or lime sinter surfaces on concrete or plaster are pretreated only if really necessary with a fluorosilicate etching liquid to reduce absorption. Where highly absorbent or an evenly absorbed substrates are encountered, it is recommended that a diluted silicate emulsion paint or a special silicate emulsion primer as shown in the following formula should be used:

Ingredient	Mass %
Water	69.5
Styrene acrylate emulsion (e.g. BASF Acronal™ S 559 or S620; Alberdingk SC 4400 or AS 6800; Celanese Mowilith™ DM 6119 or DM 765A)	0.5
Stabilizer (e.g. Woellner Betolin™ A11)	0.5
Potassium silicate (e.g. Woellner Betolin™ K28, P35 or P50)	20.0
TOTAL	100.0

Table 11

Depending on substrate conditions, a 1:1 dilution with water, or a mixture 1 part water/ 1 part primer / 1 part silicate emulsion paint may also be applied. It should be applied preferably using a brush. Generally, one coat of silicate emulsion paint is applied by brush or paint roller, waiting at least 12 hours after application of the silicate primer.

Whilst silicate emulsion paints have a very high gas permeability, they also have a very high water absorption. To therefore minimize/prevent absorption of water onto the cured silicate emulsion coating, the addition of a water repellent is recommended, or an additional impregnation with water repellent is applied as the last coat. The water repellent should only be included in the final coat, or else this may give rise to adhesion problems when subsequent coats are applied.

The most suitable weather conditions for the application of 1-K silicate emulsion paints and plasters are:

- Temperatures between +5 and +25°C (during and at least 48 hours after application)
- Moderately high relative humidity (but no rain)
- No strong sunshine heat on the walls
- No dry warm wind

Where for reasons of geography or other reasons it is impossible to ensure such situations as the above, certain application methods or adjustments to the formulations may be required to overcome any difficulties.

The properties of appropriately applied and cured silicate emulsion paint coatings compared with other systems are shown in Tables 12 and 13.

Selection Criteria for the Application of Various Coating Systems (Part 1):

Property	Area	Emulsion Paints (A)	Limewashes (B)	1-K Silicate Emulsion Paints (C)
Cost	Commercial	Inexpensive	Inexpensive	Inexpensive
Binder	Coating property	Polymer Dispersion	Lime	Potassium Silicate + Polymer Dispersion
Manufacturing	Coating formulation	Easy, possible without experience	Easy, possible without experience	Easy for expert, take note of high alkalinity
Pigment Types		Almost unlimited	Inorganic pigments	Inorganic pigments
Coating Property		Thermoplastic to elastic	Rigid	Rigid
Odour		Nil to high odour, dependent on dispersion type and formulation	Nil odour	Nil to low odour
Hiding Power		Good hiding power, dependent on formulation	Low hiding power	Good hiding power, dependent on formulation
Suitable substrates	Coating application	All surfaces except lime plaster	Primarily mineral substrate	Primarily mineral substrate (but with appropriate formulation)
Suitability on Concrete		Set concrete surfaces (not until after 28 days curing)	Not known	Fresh or set concrete surfaces
Unsuitable substrates		All surfaces except lime plaster	Exposed and aerated concrete, brickwork, and sand-lime bricks	Particle boards, existing oil paintings, fatty or oily or strongly soiled surfaces
Water release		Very slow	Fast	Fast
Temperature Restrictions		Best applied at temperatures between 5-30°C	Not known	Best applied at temperatures between 5-30°C
Penetration of binder into mineral substrate	Uncured coating property	Almost none	Almost none	Up to 6-7 mm
Fixing and Reinforcing Capacity for structure		None to low	None	Moderate to good

Table 12

Selection Criteria for the Application of Various Coating Systems (Part 2):

Property	Area	Emulsion Paints (A)	Limewashes (B)	1-K Silicate Emulsion Paints (C)
Bonding Type	Cured Coating Property	Adherent film on substrate	Cohesive weak physicochemical bonding to substrate	Cohesive strong physicochemical bonding to substrate
Coating Property		Thermoplastic to elastic	Rigid	Rigid
Flexibility		Good flexibility, dependent on dispersion type and formulation	None	Slight flexibility, can be regulated within certain limits
Covering of Capillary cracks		Fairly good	No elastic covering, but filling of fine cracks	No elastic covering, but filling of fine cracks
Water and Driving Rain Resistance		Good to very good	Low	Good
Capillary Water Absorption		Low	High	Low
Water Vapour Permeability		Low	High	High
Carbon Dioxide Permeability		Low	High (no effect on carbonation reaction)	High (no effect on carbonation reaction)
Weathering Resistance		Dependent on dispersion type and formulation	Poor	Good weathering resistance depends on silicate type
Ultra Violet Resistance		Dependent on dispersion type and formulation	Good UV resistance	Good UV resistance
Fading resistance		Good fading resistance, dependent on dispersion type and formulation	Very good fading resistance	Very good fading resistance
Solvent Resistance	Cured Coating Property	Poor to good solvent resistance, dependent on dispersion type and formulation	Good solvent resistance	Good solvent resistance
Acid Rain Resistance		Good acid rain resistance, dependent on dispersion type and formulation	Poor acid rain resistance	Good acid rain resistance
Dirt pickup		Low to high, according to recipe respectively binder	Low to high, according to recipe	Low
Chalking resistance		Good to very good	Excellent	Good to excellent, depends on silicate type
Scrub resistance		Good to very good	Poor	Good to very good
Angle of brightness/ Appearance		Adjustable across formulation	Matt finish “naturally” shaded	Matt finish “naturally” shaded
Overpaintability		Can be overpainted with (C)	Can be overpainted with (C)	Can be overpainted with (C)

Table 13

In addition to the properties of cured paint coatings such as appearance and mechanical strength etc, which allow focus on the area of water absorption and water vapour permeability. These are relevant to the heat insulation properties and heat exchange behaviour of the wall system. To prevent buildup of humidity in the exposed exterior wall, it is necessary that any moisture absorbed during a rain period is quickly and totally released again during dry periods. The German standard DIN 18 558 defines that the product of the water absorption coefficient, w ($\text{kg}/\text{m}^2\text{h}^{0.5}$) and the water vapour diffusion resistance coefficient s_d (m) should be lower than 0.2 ($\text{kg}/\text{mh}^{0.5}$).

Thus, $w \times s_d < 0.2$ ($\text{kg}/\text{mh}^{0.5}$).
and $w < 0.5$ ($\text{kg}/\text{m}^2\text{h}^{0.5}$)
and $s_d < 2$ m.

This applies to polymer improved plasters claiming good rain resistance.

For external walls which are exposed to severe driving rain, to provide good protection, $w \times s_d < 0.1$ ($\text{kg}/\text{mh}^{0.5}$).

In order to meet both of these conditions both properties must be well adapted to each other. Generally, the water absorption coefficient, w of silicate emulsion paints in category II (water repellent) range from 0.1 - 0.5 $\text{kg}/\text{m}^2\text{h}^{0.5}$. Where additional water repellent has been applied then they will come in category I (water impermeable) with water absorption coefficient, $w < 0.1$ $\text{kg}/\text{m}^2\text{h}^{0.5}$.

As regards water vapour diffusion resistance coefficient s_d , this is typically for silicate emulsion paints in category II (water vapour permeable) and range from 0.1 - 0.5 m.

Suitable formulation and application of silicate emulsion paints can meet the above conditions.

Finally, it is appropriate to comment that the water absorption coefficient is deeply influenced by the type and amount of:

- Inorganic binder (potassium silicate)
- Organic polymer dispersion
- Water repellent

The above are demonstrated in Figures 14, 15 and 16 below:

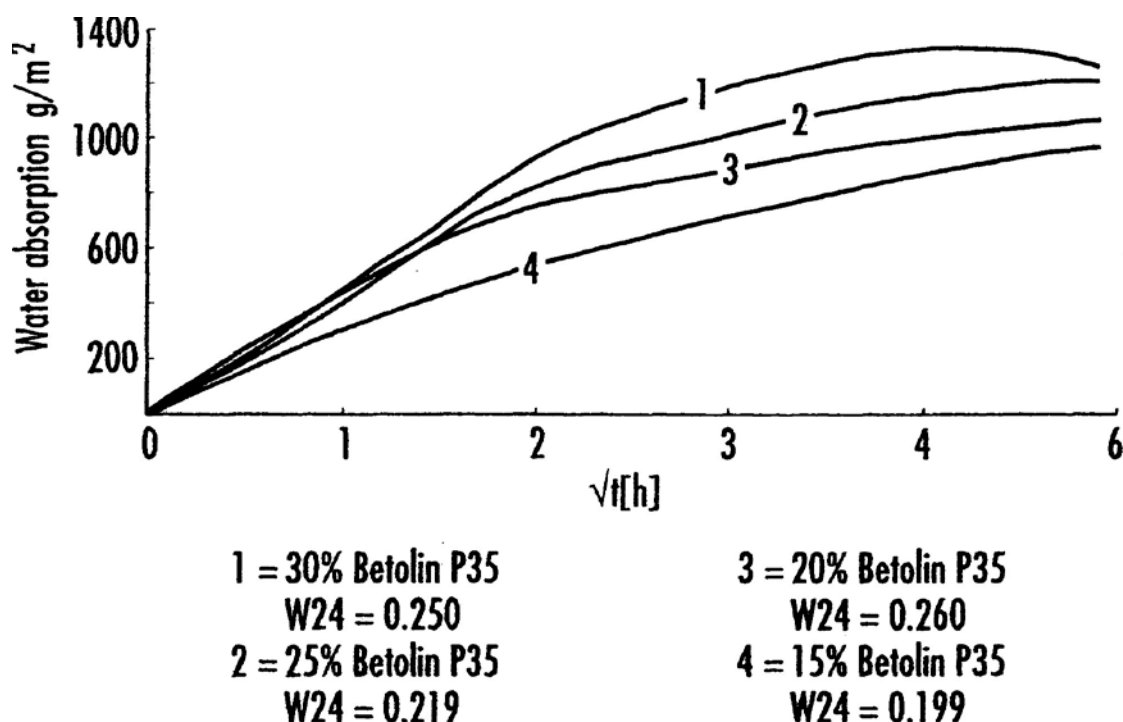


Figure 14

As can be seen, an increase in potassium silicate concentration results in increases in water absorption of the 1-K silicate coating system.

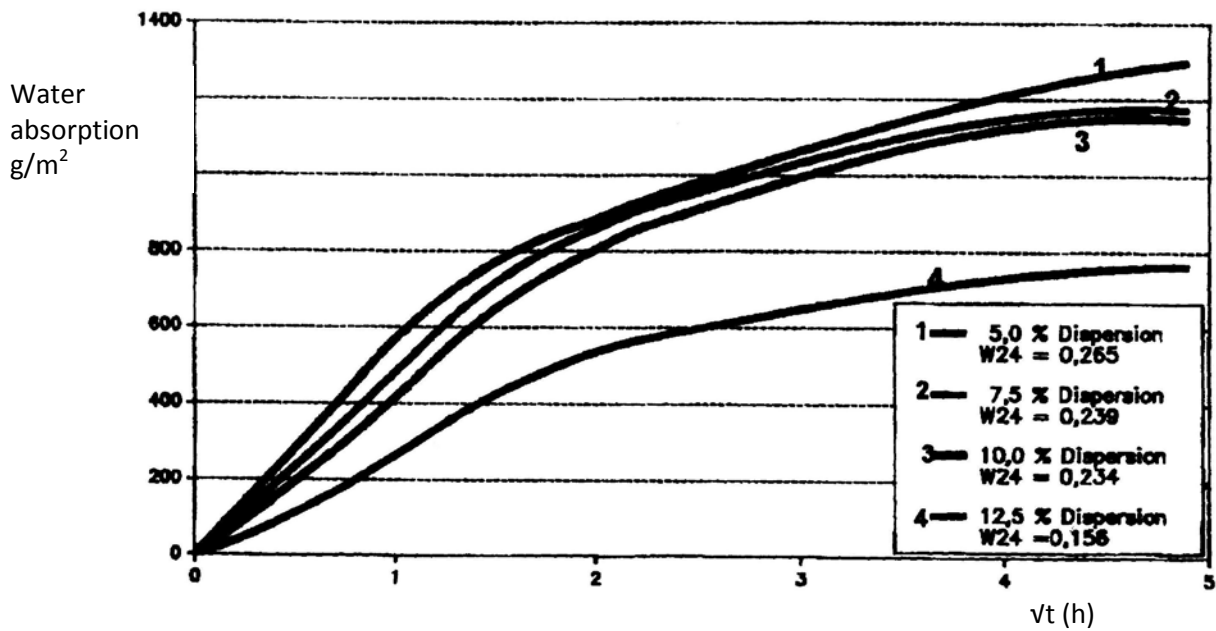


Figure 15

As can be seen, an increase in organic polymer emulsion concentration results in decreases in water absorption of the 1-K silicate coating system.

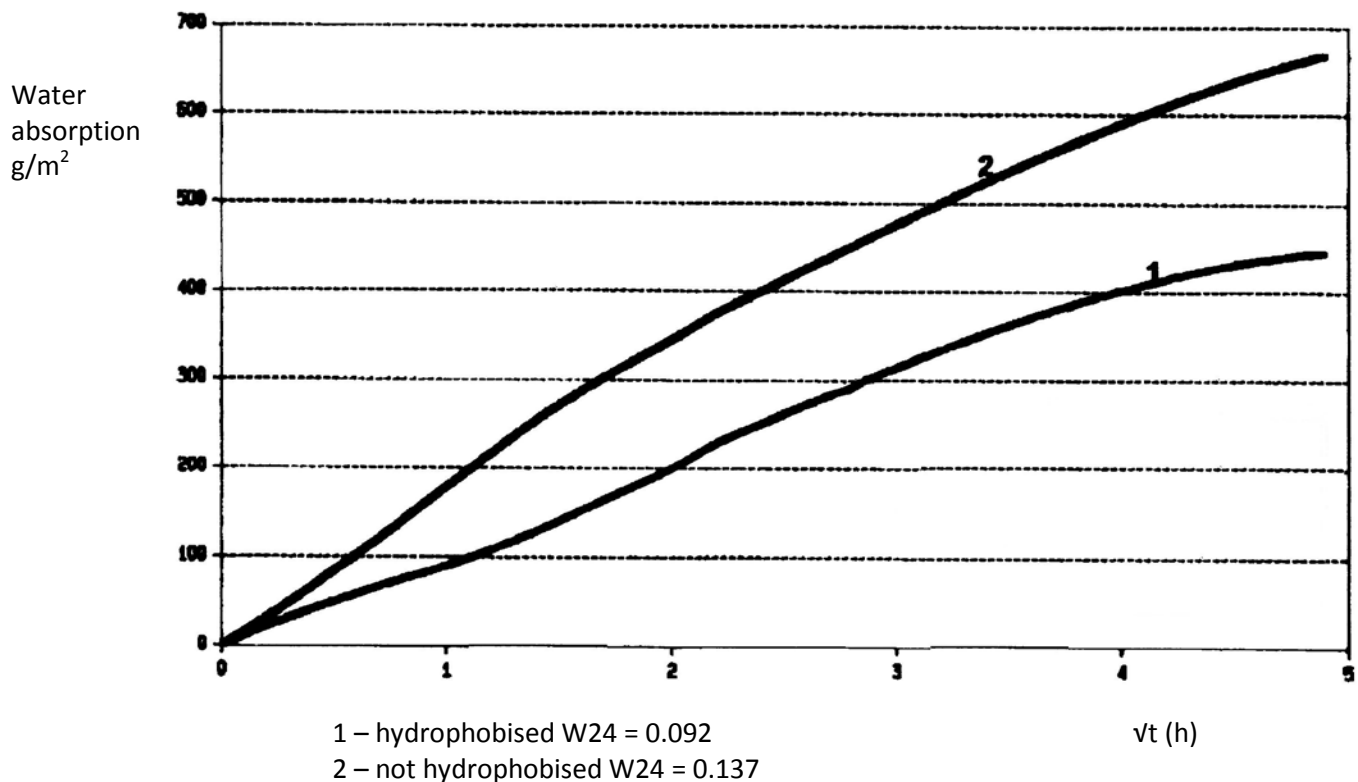


Figure 16

The last graph in Figure 16 shows the reduction in water absorption when water repellent is included in the silicate emulsion paint formulation (the lower curve showing the effect of incorporation of water repellent).

12.1.2.5. Ignition and fire resistance behaviour of silicate emulsion coatings and plasters.

Generally, according to German standards, coatings with thicknesses below 0.5 mm are not subject to classification in different classes of flammability. So, the flammability of silicate emulsion paints usually do not have to be considered. However silicate emulsion plasters, particularly where used for interior applications, need to be considered because their thickness is typically greater than this.

Depending on the total content of organic materials, silicate emulsion plasters are either classified in:

- class A2: non-flammable construction materials (lower contents of organic additives)
- or in
- class B1: hardly flammable construction materials (somewhat higher contents of organic additives).

No indication exists that silicate emulsion plasters have in any case aggravated an outbreak of fire or that serious quantities of noxious gases have been evolved. Because the proportion of organic materials in silicate emulsion paints and plasters are significantly lower than that in standard emulsion paints or plasters the potential hazard is significantly lower, and might even be considered as negligible.

12.1.2.6. Main advantages, preconditions and restrictions of silicate emulsion paints and plasters.

- The main advantages of 1-K silicate emulsion paints and plasters are:
 - Ready-to-use products
 - Good storage stability with long shelf life
 - Fairly easy application with good workability
 - No significant health risk during application
 - No allergenic potential from silicate binders
 - Zero VOC systems may be formulated using zero VOC organic emulsions
 - Applicable to a wide range of substrates (Sometimes pretreatment may be necessary)
 - Also compatible with relatively fresh plasterings containing active alkalinity
 - Appropriate for interior and exterior application on new and old buildings
 - Adequate technical properties of the cured coatings
 - Fixing and reinforcement of mineral substrate structure
 - “Natural” looking matt surface appearance with good colour stability
 - Open pore character of cured coating with excellent water vapour permeability
 - Low tendency of dirt pickup, self-cleaning behaviour
 - Good heat insulation properties of wall systems
 - Long term stability also under varying humidity of the substrate leading to a good economic lifetime
 - High resistance against atmospheric influences
 - No special hazard in case of fire
 - Acceptable cost level
 - High ecocompatibility
- The main preconditions and restrictions of 1-K silicate emulsion paints and plasters, which should be observed are:
 - Scrupulous selection and examination of raw materials
 - Careful formulation and testing
 - Appropriate instruction concerning application
 - Critical selection, inspection and if necessary pre-treatment of substrates
 - Protection of alkali susceptible areas (glass, lacquered surfaces, anodized aluminium etc.)
 - Conditions for correct curing must be attainable
 - Coatings are not flexible and so therefore should not be applied on flexible substrates

12.1.3. Silicate emulsion primer.

We discussed earlier the use of silicate emulsion primers on highly absorbent substrates or substrates with varying absorption. Another application for appropriately formulated silicate emulsion primers is for the consolidation of friable or weakly bound substrates, which may be encountered under a variety of circumstances, especially with old, weathered substrates. In such situations, a silicate emulsion primer with its high depth of penetration may be used to consolidate the substrate prior to overcoating with a silicate emulsion paint or plaster or even an organic emulsion paint or plaster. Where appropriately formulated silicate emulsion paints or plasters are used as the coating systems, then water vapour permeability would normally be maintained. However if the top coats are organic emulsion paints or plasters, then because of the closing of the pores in the coating during film formation it would be expected that water vapour permeability would be significantly reduced.

Nevertheless, the use of silicate emulsion primers could present an interesting concept to solving the problem of application of many coatings (both film forming and non-film forming) on to friable or weak substrates, since generally with film forming coatings such as organic emulsion paints they do not penetrate to anywhere near the same extent as silicate emulsion systems. Although other consolidants may be used for friable substrates, such consolidants are generally solvent borne systems or systems which have such low flashpoints that they fall within Dangerous Goods classification. A significant advantage of silicate emulsion primers in this regard is that they provide the consolidating effect, but are waterborne with the advantages of water cleanup and no flashpoint concerns. In addition, they probably represent the only choice for a relatively inexpensive waterborne consolidating system which can be factory prepared and have an extended shelf life in comparison with other water miscible consolidants. In general, we would recommend the use of potassium silicates as the inorganic binder of preference in silicate emulsion primers, since as discussed earlier the use of sodium silicates in this application could lead to high levels of efflorescence with implications for the performance of the top coats.

Finally, for those who are looking for further reading on the subject of silicate emulsion paints and plasters, there is an excellent 569 page German book by Schultze on this area.

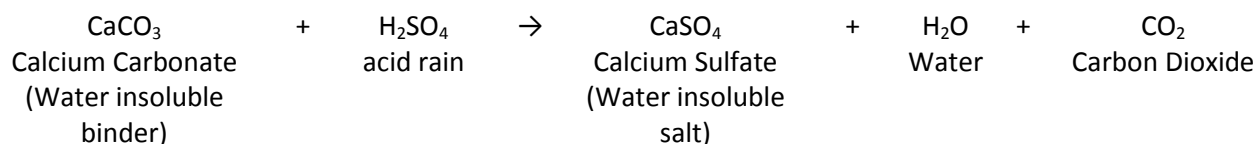
12.2. Impregnation of masonry substrates using alkali silicates.

Alkali silicates may be used for impregnation of a variety of siliceous masonry substrates including stone and concrete.

12.2.1. Impregnation of stone using alkali silicates.

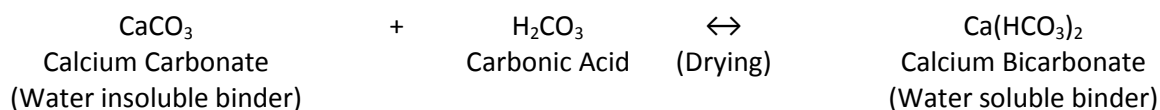
Natural stone, by its very occurrence has a longevity spanning millennia; otherwise we would not be able to find it in its natural state. However, over periods of time, environmental effects can cause weathering of the stone. This can be of particular concern as natural stone has been used to build carved items such as monuments etc. since if they go unheeded the environmental effects can cause such destruction of the stone carving that its appearance is impaired or even completely destroyed. In some natural stones the binder is calcium carbonate (which is relatively insoluble in water) and which under exposure to acid rain is converted to gypsum or calcium sulfate (which although still being relatively insoluble in water is more soluble than calcium carbonate) and can be leached out from the stone.

As a result of this loss of binder (which tends to be particularly prevalent just below the surface), the stone gradually loses its strength over time and the outside crust can spall off. This is chemically represented as follows:



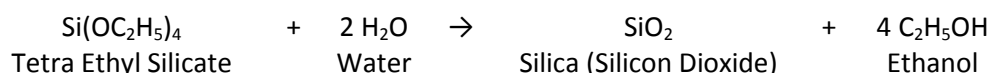
Equation 15

The water and carbon dioxide (both freely available in the atmosphere) combine to form carbonic acid, H_2CO_3 . The carbonic acid can also react with the calcium carbonate binder as follows to produce calcium bicarbonate (which is soluble in water) and can be leached out from the stone:



Equation 16

To replace the leached out binder with silica, silicates may be used. Over many years, stone consolidants based on organic silicates such as tetra ethyl silicate have been used. As described earlier, the silicate binder is produced by the tetra ethyl silicate reacting with water, with ethanol being produced as a by-product, as shown below:

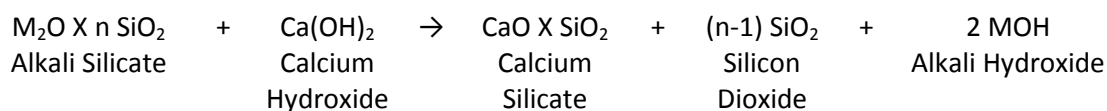


Equation 17

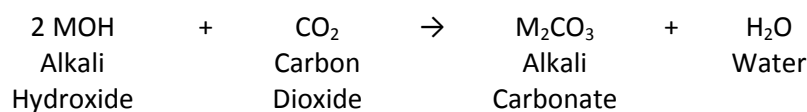
In former times, these products were typically solvent borne systems, but a major global manufacturer of stone consolidants has produced a solventless system. Nevertheless even this solventless system has sufficiently low a flashpoint that it is deemed to be a Dangerous Good, according to the Australian Dangerous Goods Code.

Here, yet again we can see an application for waterborne alkali silicates, and because we are trying to achieve good consolidation of the natural stone substrate, but without the appearance of any efflorescence, in such applications Lithium Silicates are recommended with their advantages of ambient cure, water wash up, not being regulated as Dangerous Goods as well as the formation of no water soluble byproducts.

Again we see, as shown earlier the typical cure being the following reactions shown in Equation 18 and Equation 19 below:



Equation 18



Equation 19

12.2.2. Impregnation of concrete using alkali silicates.

Concrete is yet again another siliceous substrate, but in this situation, consolidation of the concrete may be used to increase the hardness of the concrete above what has already been achieved through the appropriate water/cement ratio. Typically, it would appear that a number of impregnations with the waterborne alkali silicate are carried out, followed by mechanical surface finishing such as diamond grinding to achieve the desired surface finish.

Sodium silicates have been used for many years and are believed to form the basis of a number of well-known products in the marketplace.

Potassium silicates with their particular advantages of less efflorescence also have a significant presence in this market.

In particular in the USA, lithium silicates appear to be enjoying a high growth rate in this market, and it would appear that a number of such American developed products are being imported into Australia.

In some formulations it is understood that silica sols are added to waterborne alkali silicates, although high ratio soluble alkali silicates are much more reactive and are preferred because they are generally expected to lead to better results in concrete hardening. Silica sols (also known as colloidal silica solutions) are solutions of colloidal silica with typical particle sizes ranging from 8-125 nm, (somewhat larger than the size of the silicate particles in waterborne alkali silicates, which are of the order of 2–3 nm). Silica sol colloidal solutions may appear nearly clear and almost colourless at the lowest particle size, and with increasing particle size and concentration may range in appearance from opalescent (say around 40 nm particle size) to milky at larger particle sizes. Their stability reduces with increased particle size.

One method of manufacture of silica sols developed by Iler and Wolter described in a 1953 patent and mentioned in Iler's textbook involves the reduction of the sodium content of sodium silicate solutions by ion exchange with H^+ ions.

Silica sols may be stabilized through the addition of alkali (such as ammonia, if no increase in sodium ions is desired). The addition of an unstabilized silica sol to a waterborne alkali silicate is expected to result in generally undesirable premature gellation, and only appropriately stabilized silica sols should be used in such applications.

Although as discussed above, formulations based on sodium silicates (with their price advantage) have been well-known for many years, it appears that potassium and lithium silicates are generally used in the area of blends with silica sols because of stability issues with formulations based on sodium silicates.

Although the particle sizes of the components of formulations of potassium and/or lithium silicates mixed with silica sols are very small, the active ingredients are only expected to penetrate concrete to depths of say 1-2 mm because the silica particles are retained on the surface and are really only effectively surface hardeners. Nevertheless, such surface hardening of concrete is desirable in a number of applications and has produced a sizeable industry for formulators and applicators alike.

Where hydrophobicity of such formulations is desired, the addition of water miscible hydrophobizing agents (e.g. waterborne alkali siliconates such as potassium methyl siliconate) is carried out.

12.2.3. Impregnation of masonry substrates for chemical damp-proofing using alkali silicates.

Typically in rising damp situations, the rising damp carries dissolved salts upwards. Due to lateral evaporation the water content reduces and the salt level increases with greater distance from the ground as shown below in figure 17.

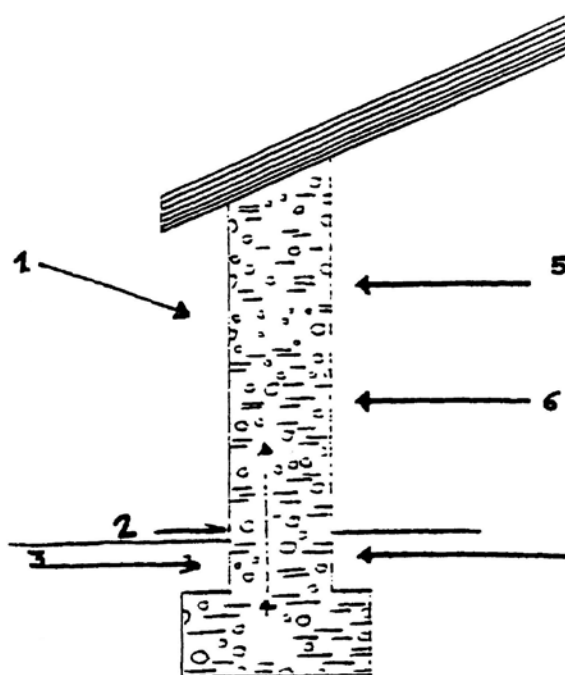


Figure 17 - Rising damp carries dissolved salts upwards

Referring to the above figure, the sources of water can be as follows:

- 1 – Driving rain
- 1 – Climatic condensation water
- 1 – Dampness from defective maintenance conditions and disposal lines
- 2 – Hose water
- 2 – Surface water
- 3 – Seepage water
- 4 – Rising damp

With increasing salt concentration efflorescence results from crystallisation of the dissolved water soluble salts. At the same time pressure builds up due to crystallisation of these salts with spalling of masonry near the surface.

Typically, such rising damp may be prevented by the use of insertion of a physical damp-course, or more recently through the use of injection of a chemical to produce a horizontal damp-course.

Potassium silicate solutions may be used in the impregnation of masonry substrates for chemical damp-proofing, normally against rising damp.

Here, potassium silicate solutions (also known as potassium water glass) are used to seal the capillaries of the dry absorbent masonry substrate consequently providing a chemical damp course barrier against water from rising damp.

Where water repellency is sought to enhance the effectiveness of the chemical damp course, water miscible hydrophobizing agents such as potassium methyl siliconate are added (as an example in a ratio of potassium methyl siliconate to potassium silicate ranging from 1:4 to 1:11 w/w).

The concentration of active substance in chemical damp-proofing formulations based on potassium silicate solutions typically ranges from 5-10%.

Typically, sloping holes (at angles of 30 to 45° below horizontal) about 12-15 cm apart are drilled into the masonry and the chemical damp course is injected, typically under the effect of gravity as shown below in figure 18.

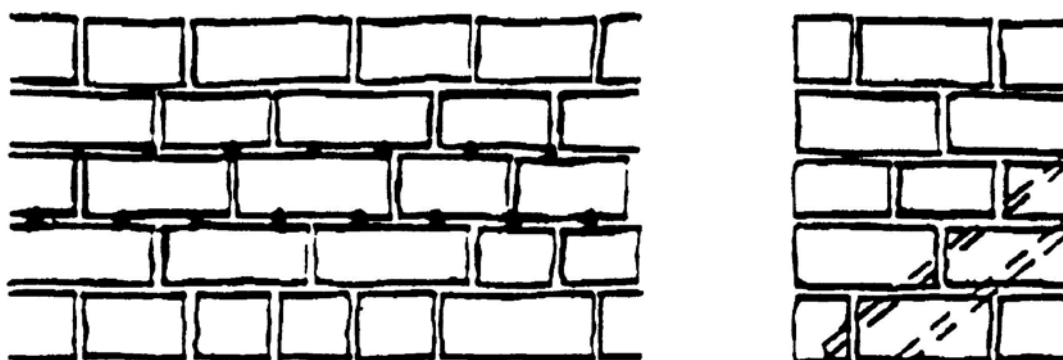


Figure 18 – Drilling Holes Arrangement for Impregnation of Masonry with Chemical Damp-proofing Liquid by Gravity Feed.

However, because the curing of the alkali silicates/siliconates require atmospheric Carbon Dioxide the formation of active ingredients is relatively slow and may even be unsuccessful where the masonry is saturated with more than 50% water content.

Other chemical damp-proofing formulations are available such as those based on silanes, siloxanes, acrylic resins and metal stearates are available, but these contain solvents which suffer from the disadvantages of being Dangerous Goods on the basis of flammability. At the same time the solvents in such solventborne chemical damp-proofing systems have a residence time in the treated masonry substrate such that human occupancy of the treated building should be delayed until all traces of residual solvent have disappeared. There is no such restriction with potassium silicate solutions (with or without water miscible hydrophobizing agents) since the only carrier used is water.

13. Ecotoxicity.

We would suggest that waterborne alkali silicates are harmless to the environment on the basis that:

- Essentially, the finished cured products produced are silicate based, as we said at the beginning of this paper, in Nature, it is understood that more than 95 volume % of the earth's crust is composed of quartz and a few rock-forming silicates. So, on that basis, it is as if we producing cured systems which are effectively very close to what already exists in Nature.
- According to the criteria of the Australian NOHSC (National Occupational Health & Safety Commission), now absorbed into the ASCC (Australian Safety and Compensation Council), waterborne alkali silicates are not hazardous substances.
- According to the criteria of the ADG-7 (Australian Dangerous Goods Code, 7th edition) waterborne alkali silicates are not Dangerous Goods.

As we also outlined earlier:

- No significant health risk during application
- No allergenic potential from silicate binders
- Alkali silicates are zero VOC products
- Zero VOC systems may be formulated using zero VOC organic emulsions
- A good economic lifetime of the coating (leading to less requirement to reapply the coating) due to long term stability.

14. Summary.

In this paper we have endeavoured to provide information about the production of alkali silicates, their properties, chemistry of cure and applications in a variety of coating and construction chemical systems including silicate coatings, silicate impregnations, silicate emulsion coatings and silicate emulsion plasters.

End markets for these products include architectural coatings, architectural renders, waterborne zinc rich protective coatings, masonry impregnation, waterborne consolidating primers, and chemical damp-proofing.

Silicate emulsion coatings were first introduced into the market in Europe in the 1960s, coming to prominence in the 1970s. About 10-15% of the waterbased architectural paint market in Europe is based on silicate emulsion paints. Introduction into other markets including United States of America, Asia and Australasia is occurring at the present.

With greater emphasis on reduction of VOC levels in coatings and construction chemicals, as well as their enhanced long-term durability compared with organic resin based systems, waterborne alkali silicates represent an environmentally friendly way of coating and consolidating masonry surfaces.

15. Acknowledgments.

We would like to acknowledge the assistance of Dr Joachim Krakehl of Woellner GmbH & Co. KG in Ludwigshafen, Germany in the preparation of this paper.

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